SUBSURFACE DOLOMITIZATION AND POROSITY OCCLUSION WITHIN EARLY TO MIDDLE ORDOVICIAN STRATA OF THE ILLINOIS BASIN, USA

BY

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THESIS

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ABSTRACT

Analysis of sedimentological, stratigraphic, paragenetic and geochemical characteristics of samples from the Early Ordovician Shakopee Dolomite and Everton Formation, and the overlying Middle Ordovician St. Peter Sandstone, obtained from drill cores and outcrops in the Illinois Basin indicate that subsurface dolomitization locally reduced primary porosity, and that the degree of reduction changes with location. Specifically, porosity occlusion by dolomitic cementation is pronounced in the Shakopee and Everton on the northern shelf of the basin, and, increases progressively to the south into the deeper part of the basin.

Three sample locations were selected for this study based on relative paleoceanographic position along a north-south transect through the Illinois Basin. These include: (1) core from the shallow marine shelf in Stephenson County (UPH well); (2) hand samples from the LaFarge Quarry in LaSalle County; and (3) core from the deep marine basin in White County (Superior Well). Quartz arenites of the St. Peter overlie the Shakopee at the post-Knox unconformity (an erosional surface) in the northern Illinois Basin. The Shakopee is a fine-grained dolomite interlayered with thinly bedded shales and siltstones. In the southern, deeper portions of the Illinois Basin, the St. Peter directly overlies the Everton . Here, the Everton is a near-shore dolomitized marine deposit containing irregular lenses of quartz sands. Previous biostratigraphic correlation studies in the southern end of the basin suggested that the Everton is age-equivalent to both the Shakopee and the St. Peter in the basin, and thus, that the post-Knox unconformity underlies the Everton. My studies of sedimentologic composition and diagenetic alteration suggest, however, that the Everton belongs within the Knox Supergroup instead of the Ancell Group, and thus that the top of the Everton is the post-Knox unconformity. Of note, cementation and lithostratigraphic characteristics at the post-Knox unconformity makes the surface act as an efficient aquitard.

A suite of 61 polished thin sections were analyzed petrographically in plane light, polarized light, and with cathodoluminescence (CL). Use of CL allowed identification of an early quartz cement and two dolomite cements (D1 and D2) that are separated from later dolomitization events by a dissolution event. A pink-red CL dolomite (RD1)

replaced D1 and D2, which is followed by a third non-luminenscent dolomite cement (D3) and a later anhydrite cement. Two late replacement dolomite cements (RD2 and RD3), which exhibit dark red and yellow-orange luminescence respectively, replaced all of the prior dolomite cements. This observed paragenetic sequence was capped by the precipitation of a late bright blue quartz cement. Covariation modeling of $\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ is consistent with the dolomitizing fluids having been formed from seawater-derived brines that were partially diluted with meteoric fluids that gained radiogenic Sr from either the Precambrian granite-rhyolite basement or from Paleozoic shales. The various cements, which reflect the consequences of successive diagenetic events, significantly reduced porosity locally.

Comparison of thin sections from the three sample localities used for this studies indicates that porosity decreases progressively from north to south in the Illinois basin. Specifically, the Shakopee, Everton and St. Peter deposits have between 10% and 30% porosity in samples from the UHP well, whereas they have only 1-5% porosity in the Superior well. This change suggests that cementation was greater in south, where diagenetic fluids were hotter and contained relatively more dissolved minerals. As these fluids migrated northwards, they progressively lost their mineral content, and thus were less capable of precipitating cements when they reached the northern shelf of the basin. Therefore, strata of the northern portion of the basin are likely better targets for subsurface CO_2 sequestration than are those to the south.

To My Parents: James and Beverly, you are my rock and my shield.
And to my sister, you are my light.

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INTRODUCTION

Knowledge of the timing, source and composition of the subsurface brines that caused dolomitization and associated porosity reduction within the uppermost Shakopee Dolomite and Everton Formation (Early Ordovician Knox Group), as well as the lowermost St. Peter Sandstone (Lower Ordovician Ancell Group), will strongly influence the development of several major projects focused on these lithologies within the Illinois Basin (Fig. 1). These include ongoing activity in hydrocarbon exploration (Bear 1997 and Gooding 2005), carbon capture and storage (CCS; U.S. DOE ATLAS 2010), and aquifer stewardship (Kolata and Nimz 2010). A comprehensive study has therefore been conducted across the unconformity between the uppermost Knox Group and the lowermost Ancell Group, known as the Sauk-Tippecanoe sequence boundary or the post-Knox unconformity (Fig. 2).

The goal of this study has been to reconstruct the relative timing, source and composition of the diagenetic waters that altered the Early to Middle Ordovician Shakopee, Everton and St. Peter in the Illinois Basin. A variety of techniques in sedimentology, stratigraphy, petrography and geochemistry have been applied to determine: (1) the sedimentological composition and associated vertical and lateral variations of these Middle Ordovician reservoir rocks; (2) grain-scale variations in $\delta^{13}C$, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ composition; and (3) the depositional and diagenetic history of each lithology. Three sample sites (Fig. 3) were first chosen to establish a paleobathymetric depositional transect from shallow-water environments on the northern shelf of the Illinois Basin, to a basinal deep-water location (Fig. 4). They were also chosen because they represent different distances, relative to the source of diagenetic fluids, at the time of diagenesis. Cathodoluminescence petrography and geochemistry trends were then established and interpreted within the paleobathymetric framework (Fig. 5). Results were then integrated, modeled and synthesized to reconstruct the multiple geological events that have culminated in subsurface dolomitization and porosity occlusion.

PROJECT CONTEXT AND GEOLOGICAL SETTING

A major carbon capture, transport and storage (CCS) research program is currently being conducted in the Illinois Basin by the Midwest Geological Sequestration Consortium (MSGC; http://sequestration.org/), which is led by the Illinois State Geological Survey (ISGS) and is primarily funded by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL). The national DOE Carbon Sequestration Program involves three key elements that involve field-testing and development. These include: (1) research and development programs; (2) infrastructure development; and (3) global collaborations. The "infrastructure component" includes the Regional Carbon Sequestration Partnerships (RCSPs) and other large-volume field tests where validation of various CCS technology options and their efficacy are being confirmed (U.S. DOE Atlas 2010).

To date, the target for these CCS activities in the Midwest have been the saline sandstone reservoirs comprising the Cambrian Mt. Simon Formation (U.S. DOE Atlas 2010). Although younger Paleozoic saline reservoirs within the Illinois Basin could potentially serve equally effective CCS target reservoirs, little has been known of their porosity and permeability characteristics (Bethke 1992). Therefore, the present study has been undertaken in collaboration with the ISGS to reconstruct the depositional and diagenetic history of the Ordovician Shakopee Dolomite, Everton Formation and St. Peter Sandstone within the Illinois Basin, as a means to evaluate their potential future use as CCS storage reservoirs.

The Illinois Basin is an interior continental (intracratonic) sedimentary basin, which covers approximately 284,900 km^2 (Fig. 1; Buschbach and Kolata 1990, Leighton et al. 1992). This basin covers most of Illinois and portions of adjacent states. Research suggests the Illinois Basin initiated above a failed rift during the Proterozoic and continued to subside through the Paleozoic, during which time is accumulated the sediment present today (Buschbach and Atherton 1979, Kolata 1994, Marshak and Paulsen 1996; Fig 3). Distinct subsidence pulses during the Paleozoic provided most of the space for sediments filling the basin. Originally, the basin was open to the south. But uplift of the Pascola Arch delineated the southern end of the basin toward the end of the

Paleozoic. Reactivation of faults led to the uplift of the La Salle anticlinorium, a north-south-trending belt of deformation the runs up the axis of the basin as well as to other fault-and-fold zones. These structures dictated the sedimentology and stratigraphy of the formations deposited within (Kolata and Nelson 1997, Pitman 1997, Marshak et al. 2000).

Subsidence rates, in general, were greater in the southern part of the basin. As a consequence, water depths at the time of deposition tended to be greater in the southern part of the basin. Due to the nature of the structure of the Illinois Basin and variable subsidence rates, a condensed version of the stratigraphic column exists in the north, while the full stratigraphic section is observed in the south. Thus, shallower-water, thinner sedimentary units of the northern end of the basin correlate with deeper-water, thicker units to the south. Because of this variation, a north-south sampling transect in the Illinois basin can encompass the basin margin, shelf and floor (i.e., a shallow to deep-water paleobathymetric transect; Fig. 1 and Fig. 5). This shallow to deep-water paleobathymetric transect helps identify if paleobathymetry at the time of deposition is the key factor controlling diagenesis (due to original rock composition, porosity, and permeability), or, if it is due to proximity of the diagenetic fluids, or, if it reflects fluid temperature and saturation. Three sites along this transect were selected for a study of diagenesis: (1) a well in Stephenson County near the Wisconsin-Illinois border; (2) the LaFarge Quarry in LaSalle County; and (3) the southern Ford well in White County. The St. Peter and Shakopee were sampled from Stephenson and LaSalle Counties. The St. Peter and Everton were collected from White County (Fig. 4).

Sloss (1963) and Kolata (1990) divided Illinois Basin strata into sedimentary sequences separated by regional unconformities, which represent periodic transgressive and regressive cycles (Fig. 2). This investigation focused on the Sauk/Tippecanoe I sequence boundary that divides the Early and Middle Ordovician. The Sauk/Tippecanoe I sequence boundary is an unconformable contact between the Shakopee and the St. Peter to the north. Due to the lowstand deposition of the Everton, (which pinches out to the north), and the full stratigraphic section preserved in the deeper part of the basin, the contact is gradational in the south between the Everton and St. Peter (Smith 1996 and

Barnes et al. 1996). The strata below the contact comprise the Knox Group, so the contact is also known as the post-Knox unconformity.

The Shakopee is a light gray argillaceous to pure fine-grained dolomite containing shale, siltstone and sandstone lenses, and which thickens to the south (Willman and Templeton 1952; Smith et al. 1993). The unit contains rip-up breccias, mud cracks, and algal stromatolites are common features, suggesting it accumulated in a very shallow water environment of deposition. The Shakopee belongs to the Canadian Series, Sauk Sequence and the Knox Dolomite Supergroup (Austin 1970). It varies in thickness from 0-2500 feet (0 - 760 m; Fig. 6). In the north, its upper contact is an unconformity at the base of the St. Peter. The Everton is a Canadian Series formation, but the question of whether it is part of the Knox Supergroup or the Ancell Group remains under debate. It is a white to rust-red dolomite subdivided into a lower fine-grained quartz arenite and an upper argillaceous sandy dolomite (Abdulkareen 1982 and Shaw 1999). The St. Peter is the base member of the Champlainian Series, Tippecanoe I sequence and the Ancell Group. It is a friable, medium-grained quartz arenite with localized basal conglomerate (Agnew et al. 1956 and Pitman 1997). It overlies the Shakopee unconformably in the north, and the Everton conformably in the south. It was deposited in a peritidal to shallow subtidal marine environment (Fig. 8).

MATERIALS AND METHODS

Study Sites and Sampling Strategy

Three sample sites within the Illinois Basin were chosen for study. Each of these sites contain the Shakopee Dolomite or the Everton Formation, and the St. Peter Sandstone. The three locations include the Stephenson County UPH core, the LaSalle County LaFarge quarry and the White County Ford core (Fig. 4). These sampling sites were strategically chosen because they collectively represent a north-south paleobathymetric depositional transect within the Illinois Basin (Fig. 3). This shelf-to-basin transect establishes a stratal framework that has permitted the correlation of subsurface diagenetic (paragenetic) events within a stratigraphic context. In turn, strategic petrographic and geochemical analyses within this stratal framework and proximity to diagenetic fluids has permitted reconstruction of the timing and composition of the burial fluids responsible for porosity and permeability alteration in these rocks. Samples at all three locations were taken at increasing depths to fully analyze the variability within the sections, and, to build a stratigraphic framework of rock types.

The Stephenson County core, called the UPH-3 21317 well, is located at 7-28N-6E *(42°26'04"N and 89°43'53"W)* (Fig. 1). A total of 23 samples of St. Peter and Shakopee were collected from the core (Fig. 9). Depositional and diagenetic fabrics of particular interest are at and just below the Shakopee-St. Peter contact (called the Sauk-Tippecanoe unconformity; Sloss 1963), so this interval was sampled more intensively. The sample labeling scheme for this location is “UPH-depth in feet”. The currently active LaFarge-Utica Stone Company’s quarry in Utica, LaSalle County is located at *(41°19'53"N and 89°00'43"W)* (Fig. 10). A total of 15 samples were collected from the quarry (Fig. 12). However, due to quarry regulations that restricted access to the vertical quarry walls, sample depths were necessarily estimated from to within ± 10 ft (± 3 m; Fig. 14). The sample labeling scheme for this location is “LQ – sample number”. The Ford, H.C. et al., 1952 C-17 well is located at 27-4S-14W *(38°08'33"N and 87°58'39"W)* in White County (Fig. 1). A total of 24 samples were collected throughout the core (Fig. 12), with additional samples collected at and just below the Sauk-Tippecanoe unconformity (Sloss 1963). The sample-labeling scheme for this location is “SW-depth in feet”.

Rock Classification

Rocks were analyzed in hand sample and in thin section under plain-light (PL), polarized-light and cathodoluminescence-light (CL). The classification scheme of Dunham (1962) was used to name the dolomitized carbonates. This classification is based on depositional texture and depends solely on whether the limestone is matrix-supported, grain-supported or has been so extensively recrystallized that the original fabric is no longer distinguishable. The classification scheme of Williams et al. (1982) was used to classify the sandstones on the basis of three mineral components. This classification is based on the mineralogical and lithologic composition of the grains (i.e. quartz, feldspar lithic fragments) and the grain-to-matrix ratio.

Microscopy

A total of 61 standard-size, 32 µm-thick, polished, uncovered thin sections were prepared by National Petrographic Service, Inc. (5933 Bellaire Blvd, Suite 108, Houston, Texas; http://www.nationalpetrographic.com/). Thin sections were analyzed under plane light and polarized-light on a Nikon PhotoPol research-grade microscope for sedimentological descriptions. Each thin section was then analyzed under plane light [Sam -- it's not clear if PL is plane or polarized, since both start with 'P' -- which do you actually use.] and CL on a Nikon PhotoPol research-grade microscope (Fouke and Rakovan 2001). Each thin section was scanned and printed out to create a map of the thin section. Specific locations of interest were photographed and marked on these maps for easy identification and relocation of individual components.

A RELIOTRON III Cathodoluminescence microscope stage (Relion Industries (PO BOX 12, Bedford, MA; http://www.excitingelectrons.com/) was used for CL analyses. The Relion stage has a cold cathode electron gun that bombards the surface of well-polished thin sections with an electron beam in a moderately-high vacuum (Relion 2009). Beam voltage and beam current during analysis was 7-10 kV and 0.5-1.5 mA, respectively. Images were acquired using a thermoelectrically cooled Optronics DEI-

750T camera that allowed for lengthy exposure times with minimal visual variance and resolution of 768 X 494 pixels (Fouke and Rakovan 2001). These image were then sent to a video mixing board which routes the image to a Mac Pro computer. Final Cut Express 4.0 (Apple Inc.; http://www.apple.com/finalcutpro/) video editing software was used to capture and save high-resolution still images from the video signal.

Microdrilling for Geochemical Analysis

Plane light, polarized light and CL petrography was used to identify the paragenetic events that were specifically targeted for microdrilling and isotopic analyses. After locations were targeted in the hand samples for sampling a hand sample map was created for each hand sample for later reference. Prior to drilling, each hand sample was cleaned under running water, allowed to thoroughly air dry and was then photographed. The hand sample was then placed under a binocular scope on clean weighing paper. Microdrilling was conducted on a Nikon UFX-IIA stereoscope with 2 to 3.5X zoom capabilitiy, mounted with a CUDA Model 1-150 light ring attachment system. An XL-030 electric drill (Osada Electric Co., LTD; http://www.osada-electric.co.jp/English/) and outfitted with a diamond impregnated number 14 drill burr (bit; Brassler USA; http://www.brasselerusa.com/home.htm) was successively submersed in 1% HCl, MiliQ water and Ethyl-Alcohol for 15 seconds to clean the drill burr between each sample location. Each drill position was first marked on the hand sample, then marked on the hand sample photograph and then drilled briefly to “poison the tip” of the drill burr. The tip is considered "poisoned" because impurities have collected on the rock sample during preparation and would contaminate the results if not removed by drilling the surface and removing the uppermost mm of the sample. The sample powder liberated from each drill hole was then brushed onto clean weighing paper and transferred into two separate 1 ml glass centrifuge vials with plastic screw caps. One vial was dedicated for carbon- and oxygen-isotope analyses, while the other vial was dedicated for strontium-isotope analyses. Although this technique is more accurate than bulk-rock sampling, the drill bits were large enough that sampling of other events and impurities mixed in with the target area of the hand samples. Preventative measures were taken to reduce this contamination as much as possible by identifying areas of least variability in the hand samples with CL.

Carbon and Oxygen Isotopic Analysis

Microdrilled powder samples were delivered to the ISGS for carbon- and oxygen-isotope analysis. The isotopes were measured by the analysis of CO_2 released during digestion of 40 to 130 μg of sample powder in 100% phosphoric acid at 70°C on a Finnigan Mat 252 isotope ratio mass spectrometer with an attached Kiel III Individual Acid Bath Carbonate Device. The resulting ^{13}C and ^{18}O values are reported relative to the Vienna Peedee belemnite (VPDB) reference in per mil notation. The standard was calibrated through analysis of NBS-19 with values of 1.95‰ and -2.2‰, respectively (Coplen et al., 1983). Six standards (NBS-18 and NBS-19) were run with the sample set. The reproducibility for $\delta^{13}C$ and $\delta^{18}O$ using this equipment is typically <±0.1‰ and < ±0.15‰ respectively.

Strontium Isotopic Analysis

Microdrilled sample powders were weighed to 1 +/- 0.1 mg and dissolved in 0.05 N HNO_3 for 120 hours. Columns containing Eichrom Sr-spec resin were initially flushed twice with 0.05 N HNO_3 and then rinsed with 0.2 mL of 3 N HNO_3. A 0.5 ml split of the sample dissolved in the HNO_3 was then added to each column, followed by 0.1 ml of 3 N HNO_3. Two drops of 3 N HNO_3 were added twice, sequentially, followed by a series of four 0.3 ml aliquots of 3 N HNO_3 that bound the strontium to the resin. The columns were eluted first with 1 mL NanoPure water and then with 1 ml 0.05 N HNO_3 and collected in beakers. Half the reservoir of each column was then filled with NanoPure water to fully wash the residual strontium from the Sr-resin.

Sr-isotopes were analyzed by MC-ICPMS using a Nu Plasma HR located in the Department of Geology at the University of Illinois at Urbana Champaign. Samples were introduced as solutions of 100 ng/ml Sr concentration into a DSN-100 desolvating nebulizer. Along with Sr isotopes, ^{85}Rb and ^{83}Kr signals were measured and assuming natural ratios, isobaric interferences of ^{87}Rb, ^{84}Kr and ^{86}Kr were subtracted off the Sr peaks. $^{87}Sr/^{86}Sr$ was calculated based on the measured $^{86}Sr/^{88}Sr$ assuming an exponential mass bias from a true ratio of 0.1194. NBS 987 was run every 5 samples and an in house coral standard was run at least every 10 samples. The running laboratory average for

NBS 987 over the time period of this study was 0.710267 +/-18. Veizer et al. (1999) report a mean NBS SRM 987 value of 0.710240 (1 sigma $\pm$0.000016). Therefore, a constant of 0.000027 has been subtracted from the data measured in this study for direct comparison with the strontium secular seawater curve of Veizer et al. (1999).

Chemostratigraphy

Stratigraphic sampling of the three localities at increasing depth allowed for analysis of isotope variation with depth as well as across the paleobathymetric transect. The ∂^{13}C, ∂^{18}O and ^{87}Sr/^{86}Sr chemostratigraphy of the Shakopee, Everton and St. Peter is summarized in Table 2 and Figs. 9, 11 and 12. Significant variation occurs in both ∂^{13}C and ∂^{18}O, with respect to an estimated seawater dolomite (ESD) composition reconstructed for the Ordovician by Land (1985) and Veizer et al. (1998). In general, both ∂^{13}C and ∂^{18}O are depleted with respect to the ESD composition, and become lighter with increasing depth. Strontium at all three sampling localities exhibit ^{87}Sr/^{86}Sr values that are significantly more radiogenic than the ESD composition (Land 1985; Veizer et al. 1998). These trends exist throughout the entire north-to-south shelf-to-basin depositional transect.

RESULTS

Sedimentology and Stratigraphy

Stephenson County

The UPH Stephenson County core penetrates the northern shelf of the Illinois Basin and was sampled at a depth of 467-599 ft (142-183 m). The core selection consists of 124 feet (37.8 m) of the Shakopee, the Sauk/Tippecanoe I disconformity and the overlying lowermost 8 ft (2.5 m) of the St. Peter (Fig. 9). The Shakopee is composed of fine to medium grained, rounded, well-sorted wackestones and mudstones, with wackestones (~40%) being the dominant lithology in the UPH Stephenson County core. Some layers are composed of 0.5 to 4 cm-scale brecciated dolomite clasts. Mm- to cm-scale reddish brown shale, siltstones and quartz arenite beds are also common (~25%) (Fig. 13). Irregular (1 mm - 0.3 cm) vugs occur on or near cm-scale micro-faults with slickenside planes (Fig. 13). Evidence for soft-sediment deformation is manifested by mm- to cm-scale ball-and-pillow structures as well as convoluted parallel millimeter-to-centimeter scale discontinuous sets of wavy bedding (Fig. 13). Grain fracturing, dissolution and solid solution affects are seen extensively in the Shakopee (Fig.13). Micro-faults and fracturing is also observed.

The top 1.5 feet (0.5 m) of the Shakopee, is a reddish brown mudstone to dolomitic wackestone, locally containing rounded quartz grains (Fig. 14). Sub-mm-scale bedding occurs in this red shale within both the upper Shakopee and the basal St. Peter. (Fig. 14). Slumping structures, rare convoluted layers and a 2 mm-thick glauconite bed occur just below the contact itself (Fig. 14). The basal 10 cm of the St. Peter, immediately above the unconformity, consists of a grain-supported quartz wacke, in decimeter to centimeter thick beds. Quartz grains in these beds are uniform in size (about 1-3 mm). They are surrounded by a matrix of very fine clay and tiny dolomite crystals. The quartz wacke beds grade upwards into argillaceous sandstones, at about 10 cm above the unconformity. These strata, in turn, grade up into the typical, tannish-white medium-grained, well sorted quartz arenite of the St. Peter (Fig. 15). Sand grains in this sandstone are well rounded, and beds are 1 to 25 cm thick.

LaSalle County LaFarge Quarry

The 105 ft-thick (32 m) stratigraphic section exposing the Shakopee and the St. Peter in the LaFarge quarry in LaSalle County (Fig. 10) was deposited on the northern shelf in a basinward position relative to the Stephenson County UPH core (Fig. 11). The quarry consists of the uppermost 95 ft (30 m) of the Shakopee, the top Shakopee Sauk/Tippecanoe I disconformity and the overlying lowermost 2 m of the St. Peter (Fig. 11). The Shakopee here in LaSalle County is time equivalent to the Shakopee further north in Stephenson County, if not older. Interestingly, the St. Peters are around the same age. The St. Peter deposited in LaSalle County is part of an off-shore barrier island, deposited at the same time as the St. Peter in Stephenson County (Willman and Templeton 1975).

The Shakopee in LaFarge Quarry varies in composition between a dolomitic mudstone, fine to medium, sub-rounded to sub-angular dolomitic wackestone, and quartz wacke (Fig. 13). Centimeter-scale silt and shale layers are rare, but hummocky when present. At many localities, quarry walls reveal exposures of 2 to 8 meter-high, massive, laterally linked hemispheroidal stromatolite beds. Fractures, fracture fill and vugs are common in all beds, but are particularly abundant in the stromatolite beds. Mud cracks and rounded lithoclasts within dolomitic and sandy centimeter scale beds also occur locally (Fig. 13). Of note, the massive stromatolite beds present in Shakopee strata exposed in LaSalle, do not occur in Stephenson County. Also, the combination of shales and soft-sediment deformation that occur in the Shakopee of Stephenson County were not observed in the LaSalle quarry (Fig. 13). Although large-scale bedding and lithologic composition is variable, the grain mineralogy, size, shape and micro-structures are similar. Breccias observed have angular 1mm to 1cm grains within dolomitic cement and are likely depositional due to horizontal bedding planes both above and below the breccia layers. Clastic dikes are found in multiple horizons in LaSalle County. They usually compose 2-9cm brecciated dolomite clasts with sandstone fill.

The sequence at the top of the Shakopee is composed of interbedded wackestones and heavily dolomitized, tan, well-rounded and sorted quartz wackes (Fig. 14). The beds are generally parallel and centimeter to decimeter scale in thickness. Some scour marks were observed, but rare (Fig. 14). Notably, the top of the Shakopee in LaSalle differs markedly from the same stratigraphic interval in Stephenson County. In LaSalle, there is shale below the contact, but in Stephenson County, there is not. Rather, in Stephenson county, a succession of dolomites and sandstones occurs below the contact. The St. Peter above the unconformity in LaSalle consists of a tannish-white, sorted, well-rounded, frosted, friable quartz arenite. Micro dolomite crystals are ubiquitous, but in trace quantities (Fig. 15). Compared with the St. Peter in Stephenson County, it is more typical of the renown industrially used St. Peter (Lamar 1928). Extensive dolomitization within the St. Peter only occurs at the basal contact (Fig. 15).

White County

The White County Ford well penetrates the center of the Illinois Basin at a subsurface depth of 7495 to 7682 ft (2285-2342 m). The core, which is the southernmost of my sample sites, consists of the uppermost 165 ft (50 m) of the Everton, the Sauk/Tippecanoe I disconformity, and the overlying lowermost 1 m of the St. Peter (Fig. 12). After deposition of the Shakopee, relative sea level dropped and remained at a low stand, during which time the Everton was deposited (Shaw 1999 and Craig 1991) The lowest member of the Everton is an argillaceous sandstone that grades upward over a 5 m interval into nearly pure dolomite. Shortly following Everton deposition, sea level rose once again , and the St. Peter was deposited. The St. Peter quartz grains in the southern end of the basin represents extensive transport from the provenance of origin and incorporate more muds than at the basin shelf due to little reworking and a fast sea level rise. Further up on the shelf, (near LaSalle County quarry), the St. Peter represents an offshore bar deposit, while on the platform, (in Stephenson County), the St. Peter represents aeolian dune deposits. The White County well is located at the boundary between the deeper-water depocenter of the Illinois basin and the basin shelf (Craig 1997). This, it provides a stratigraphic record of subtle paleoenvironmental fluxuations on the margin of the basin.

The lowermost portion of the Everton in the White County well is a white-to-red, locally argillaceous, rounded sandstone (Fig. 16). In this interval, centimeter-scale beds of sandy dolomitized wackestones and packstones are interbedded with sandstone layers and eventually dolomitic mudstones predominate. Hummocky and beds (relicts of slumping) as well as meter-scale stromatolites were observed, as were scour marks and ball-and-pillow structures. Conodont shells occur in the beds, but are rare (Fig. 16). The contact between the Everton and the St. Peter is gradational. The top of the Everton is composed of approximately 3 ft (1 m) of interbedded sandstones, siltstones and red-brown shale, which slowly grade upward into quartz wackes and quartz arenites. Some scours and fractures break up the hummocky, wavy bedding in this interval. Also, centimeter-scale nodules of anhydrite, as well as micron-scale anhydrite cements are ubiquitous throughout the interval. Due to the gradational transition from the Everton into the St. Peter, a discrete contact surface between the two units is impossible to identify in the White County well(Fig. 14). This type of contact contrasts markedly both with the obvious contact in the Stephenson County well and in LaFarge Quarry.

Above the gradational contact between the Everton and the St. Peter in the White County well, the massively bedded, well sorted, medium-grained quartz arenite of the St. Peter occurs (Fig. 15). This interval in the core appears to be heavily weathered . Quartz overgrowths and anhydrite fill the inter-granular pore space of this rock. Unlike the St. Peter deposited on the shelf margin (found in the LaFarge quarry) or in the inner-shelf platform (Stephenson well), deposits of the St. Peter in the White County well have experienced a more significant diagenesis and cementation.

Paragenetic Sequence

Plane light, polarized light, and CL petrography were used to identify and characterize the individual sedimentological and diagenetic events that have taken place within the uppermost Shakopee and Everton, and the lowermost St. Peter, and the gradational contact zone separating them. Siliciclastic and carbonate grains, diagenetic crystals, cement, porosity and permeability were examined and mapped within the shelf-to-basin depositional transect. CL study proved to be the most useful tool in this work, because different components of cements have distinct CL signatures. I have compiled the events compiled into a relative sequence, from early to late, called the *paragenetic sequence* (Breithaupt 1849). The paragenetic sequence defines the timing of events relative to each other. Isotopic analysis of different cements of the paragenetic sequence provides constraints on the source and character of the diagenetic fluids from which the cements precipitated (discussed later). A paragenetic sequence was created for each of the 61 thin sections. The paragenetic sequence was the same for all depths at each individual location, so three paragenetic sequences were compiled: one for Stephenson County, one for LaSalle County and one for White County. Careful analysis of the three compilation paragenetic sequences lead to the realization that all three localities were also comparable. Although all localities had the same exact paragenetic sequence, each event within the sequence represented different volumes of rock alteration, (namely dolomitization) based on depth within the basin and relationship to the Sauk-Tippecanoe I sequence boundary. This volumetric analysis was based on qualitative analysis of each of the 61 thin sections; grouping each event into either absent (0%), rare (1-15%), common (15-40%) and abundant (>40%). Based on correlating the depositional and diagenetic events observed at all three locations, they were compiled into a single representative paragenetic sequence (Fig. 17). These observations have been further grouped into two primary periods of diagenetic alteration, namely: (1) early subsurface burial; and (2) late subsurface burial (Fig. 17; Table 1). However, due to the ambiguity of the cross-cutting relations associated with the anhydrite, it is discussed last.

(1) Early Subsurface Burial: The first post-depositional paragenetic event produced a thin (5-25 μm-thick) dark blue CL quartz overgrowth cement (QC1) precipitated on the outer surface of the original quartz grains (Fig. 17). An early euhedral dolomite cement (D1) then formed rhombic crystals that are 5 to 100 μm in diameter (Figs. 17, 18). A second dolomite cement (D2), consisting of 10 to 30 μm-diameter rhombic crystals, then encrusted D1 (Figs. 17, 18). D1 and D2 cements were then completely replaced. However when the cements were later replaced, the outline of the original dolomite cements were kept in-tact (described below; Figs. 17, 18). The only information regarding D1 and D2 are from the remnant outline of the original crystal shapes.

(2) Late Subsurface Burial: This later stage of paragenesis initiated with pressure solution due to compaction, as indicated by the occurrence of sutured boundaries that cut across previous cements (Ds1; Fig. 17). This was followed by the precipitation of 1 to 5 μm-diameter crystals of replacement dolomite 1 (RD1) . These grains have bright pink to red mottled CL signature (Figs. 17, 18, 19, 20). The occurrence of the RD1 event

pervasively altered the D1 and D2 cements. RD1 cements were followed by the precipitation of anhedral 1 to 5 μm-diameter non-CL dolomite cement crystals (D3; Figs. 17, 18, 19, 20). Possibly around the time of anhydrite precipitation (discussed at the end of this section) two events of replacement dolomitization (RD2 and RD3) took place. RD2 event produced anhedral dolomite crystals that are 1 to 25 μm in diameter. These crystals display a mottled, dark rust-red CL emission (Figs. 17, 18, 19, 20). RD2 cements commonly replace RD1 cements, and are identifiable either as crystalline rims encrusting D3 crystals, or as precipitates within D3 crystal imperfections. RD3 cements are composed of 1 to 10 μm-diameter anhedral crystals with a mottled bright yellow to orange CL replacement fabric (Figs. 17, 18, 19, 20). Trace pyrite crystals that are less than 10 μm in diameter (Figs. 17, 19) grew after the multiple events of replacement dolomitization (RD1, RD2 and RD3). Also, late-stage, white to blue CL, euhedral to anhedral quartz cement crystals (QC2; Figs. 17, 20) precipitated as overgrowths on original quartz grains, as cement along fractures, and as pore-filling cement in mudstones, siltstones, and sandstones. The paragenetic sequence concludes with the precipitation of late 1-3 μm-diameter light pink to mauve CL dolomite crystals (D4; Figs. 17, 20). The relative abundance and isotopic composition of replacement dolomites RD1, RD2, and RD3 and dolomite cement D3 is presented in Table 2. The precipitation of deep blue to green CL anhydrite cements (An; Fig. 19) could have either occurred as the early alteration of gypsum, (deposited as an evaporite), or as a later diagenetic precipitation associated with deep fluid migration through the basin. However, the relative timing of this cement is not certain because of the lack of definitive cross-cutting relationships within the rock pore spaces. As the regional volume of anhydrite is greatest in the deep basin (~15% of the bulk rock) and lessens northward toward the shelf (~5%) and platform (~1%), it is more likely that the origin of the anhydrite is from basin fluid migration.

Modeling

Water-rock interaction and mixing modeling of diagenetic fluids (Fig. 21), in combination with chemostratigraphic trends observed in each of the three sections (Figs. 9, 11 and 12), have been used to understand the complex history of porosity and permeability evolution in the Shakopee, Everton and St. Peter. The isotopic data collected in the present study have therefore been modeled (Fig. 23) using single-stage iterative water/rock interaction and mixing equations described in Sears et al. (1975), Faure (1986), and Banner and Hanson (1990). An estimated seawater dolomite (ESD) composition for Ordovician seawater has been calculated from Veizer et al. (1999) and used as the comparative starting dolomite (D1 and D2) composition in these calculations. Diagenetic water compositions reported in Banner and Hanson (1990; and references therein) were used for the end-member diagenetic fluid compositions that recrystallized D1 and D2.

Modeling results imply that dolomite recrystallization events (RD1, RD2, RD3) as well as the late stage dolomite precipitation event (D3) are the product of both subsurface water-rock interaction and fluid mixing (Fig. 22). Covariations in □^{18}O versus □^{13}C are consistent with derivation from the subsurface mixing of an evaporated seawater-derived brine with meteoric-derived water (Fig. 21; Arthur and Anderson 1983). In addition, covariations in □^{18}O versus ^{87}Sr/^{86}Sr and □^{13}C versus ^{87}Sr/^{86}Sr (Fig. 21) indicate that these mixed waters contained radiogenic Sr, which may have been derived from either fluid mixing process or water-rock recrystallization dolomitization.

DISCUSSION AND BURIAL HISTORY

Below, I use the paragenetic history described above in conjunction with isotopic analysis to reconstruct depositional and diagenetic events that took place in the Illinois Basin, which resulted in the accumulation of sediment, and then the compaction and cementation, especially dolomitization of sediment.

Depositional History

Shakopee Dolomite

The Shakopee Dolomite contains a variety of rock types, including: (1) dolomitized crystalline limestone; (2) dolomitized mudstone; (3) quartz-rich wackestone; and (4) dolomitized wackestone. These strata are Early Ordovician in age (Sardeson 1934), based on biostratigraphic analysis. The unit becomes progressively younger to the north (Shaw 1999). The most common sedimentary structures at the two northern shelf and shelf margin locations include stromatolites, mud cracks, rounded lithoclasts, fractures, and scours (Fig. 13). Clastic dikes which likely formed during early compaction prior to lithification are also observed at multiple horizons within the Shakopee. These observations are consistent with the sedimentological descriptions of Willman and Templeton (1952) which describe the Shakopee as an argillaceous, very fine-grained dolomite with thin interbeds of medium-grained, cross-bedded sandstone. Willman and Templeton also observed medium-grained dolomite, shale and siltstone with brecciation, conglomerates, and ripple marks. Due to the stromatolites, mud cracks and rip-up-related brecciation due to slumping , it is likely that the environment of deposition was a shallow marine to near shore tidal flat (Willman et al. 1975, Smith 1996). Anhydrite precipitation within the Shakopee increases from ~1% in the northern most section to ~5% in LaSalle County.

Everton Formation

The Everton Formation is early Middle Ordovician (Whiterockian) in age, and underlies the Shakopee in the southern portion of the Illinois Basin (Fig. 4). The Everton has been separated into two members, which include: (1) a lower white quartz arenite to quartz wacke; and (2) an upper dolomitized crystalline carbonate with some argillaceous beds. Stratigraphic pinch-out toward the northern shelf limited sampling of the Everton to the White County well at the southern end of my transect (Fig. 4). In this location, the Everton contains conodonts within mm- to cm-scale interbedded muds, silts, and sands. The Everton has been extensively studied in Missouri, Tennessee, and Arkansas (Ulrich and Butts 1913; Templeton and Willman 1963). However, few wells in Illinois have actually penetrated the Everton and there are no exposures in outcrop in the state. My descriptions of the Everton in the present study are consistent with those reported by previous investigators (Abdulkareen 1982; Craig 1997; Shaw 1999), except that I also saw evidence for anhydrite crystallization in the strata, a feature that previous investigators did not see. It is likely that the Everton was deposited in shallow-marine, possibly lagoonal, environments (Craig 1991). The abundant micrites comprising the Everton (Fig. 16) likely represent deposition during relative sea level low stands (Craig 1997). Angular quartz grains with a bright blue CL are common in the Everton (Figs. 19, 20). The distinct CL signature of these grains suggest that they originated from a provenance source that was different from that of the St. Peter (Dott 1986). Furthermore, the CL fabric suggests that these grains were partially dissolved and re-precipitated as quartz overgrowths.

Sauk/Tippecanoe I Sequence Boundary

There is ongoing debate in the literature regarding whether the Everton should be stratigraphically placed within the Knox Supergroup or the Ancell Group (Ulrich and Butts 1913; Flint 1956; Templeton and Willman 1963; Shaw 1999). In the north, due to the erosional disconformity between the Shakopee and the overlying St. Peter Sandstone, there is no question that the Sauk - Tippecanoe I sequence boundary occurs between the two formations (Buschbach 1964). In addition, biostratigraphic gaps, in conjunction with valley fill and scours are observed at the contact between the Shakopee and St. Peter in the north (Fig. 15). Further south, in the deeper part of the Illinois basin, conodont studies have not revealed a biostratigraphic unconformity at the contact, and there is no evidence for an episode of erosion between the Everton and the St. Peter (Bonab 2010; Lucia 1999). (This makes sense, considering that the deeper part of the basin subsided more rapidly, so the region remained submerged at times when the margins of the basin

were exposed.) Therefore, to determine the position this boundary in the central part of the basin (the southern end of my transect)_other information is needed.
Based on the faunal content of the Everton type area in Arkansas, in combination with subsurface logging, Willman and Templeton (1975) include the Everton within the Knox Dolomite Supergroup. Conversely, based on the Everton's stratigraphic relationship to the underlying Knox Supergroup and the overlying Ancell Group, Shaw and Schreiber (1991) suggest that the Everton is not stratigraphically equivalent to the Knox. Shaw (1999) further supported his earlier claim by stating that the definition of "Supergroup" should exclude the Everton from the Knox due to a regional disconformity observed at the margins of the Illinois Basin. However, the similarity of stromatolite beds, breccias, rock types, physical rock properties and diagenetic alteration patterns observed in the present study support the proposition of Willman and Templeton (1975) that the Everton Dolomite be placed in the Knox Group. Dolomite cement type, size of the crystals and the CL signatures of the dolomites are the observable similar diagenetic alteration patterns. Thus, the Sauk/Tippecanoe I boundary should be placed below the St. Peter everywhere in the Illinois Basin, creating a consistent and widely distributed regional stratal boundary.

St. Peter Sandstone

The St. Peter is a pure, well sorted friable quartz arenite (Fig. 15) of Middle Ordovician (Chazyan) age. The well-rounded, medium-sized, frosted St. Peter grains were derived by erosion of Precambrian igneous and metamorphic rocks of the Canadian Shield. These grains have been repeatedly eroded and reworked during trangressive cycles. This explains the general uniformity of the quartz grains, lack of lithic fragments and clays, and the scarcity of fossils (Dott et al. 1986, Keith and Kemmis 2005). The Precambrian Shield lies to the north and east of the Illinois Basin, so rivers carrying the sediment into the basin would have come from the north and east. This provenance explains why St. Peter pinches out to the south and west. In the north, the St. Peter unconformably overlies the Shakopee. In the deep southern portion of the basin, the Everton Dolomite grades vertically up into the St. Peter.

Burial History

Early rhombohedral dolomite cements typically display an inclusion-rich cloudy core, followed by a clear, inclusion-free cement overgrowth of the dolomite (i.e. Cander et al. 1988). Similar dolomite fabrics were observed in the strata that I studied (Fig. 17 and 18). However, I also found the early planar dolomite was formed during two early dolomitization events (D1 and D2). Oxygen-isotope studies on δ^{18}O quartz cements (Luczaj 2006) support an early near-surface growth in meteoric waters (-10% to -5% per mil) at 10° to 30°C in the St. Peter. However, due to the complete replacement of the early dolomites, isotopic analyses of D1 and D2 were impossible to acquire.

Anhydrite observed in this study varied from cement overgrowths comprising as little as 2% of the bulk rock to the precipitation of massive cm-scale interlocking grains in the deep-basin section. However, the anhydrite's ambiguous grain boundaries with respect to other mineral phases has prevented accurate determination of the relative timing of anhydrite precipitation. It is also possible that the anhydrite is a diagenetic product of gypsum alteration, which would be consistent with the tidal-flat depositional environment of the Shakopee and Everton. The netted, "chicken wire" fabric observed in the Everton (Fig. 19) further supports this interpretation (Bonab 2010; Lucia 1999); which might imply a sabka/seepage-reflux model (Alsaran 2008) for the early dolomites D1 and D2.

Pitman (1997) analyzed the oxygen-isotopes of the quartz overgrowths within the St. Peter Sandstone, and those were used to establish a burial curve correlated with subsidence of the basin and heat advection into the basin. Direct correlation of Pitman's paragenetic sequence with this study's paragenetic sequence provided the framework with which to compare the timing of my dolomite cements with temperatures indicated Pitman's burial curve. The quartz cement event identified in both Pitman (1997) and this study served as a relative time anchor. D1 and D2 of this study occurred before the quartz cement, and was therefore placed on the burial curve prior to the quartz. Although no remaining original isotope signatures from D1 and D2 were available, this correlation makes it possible to reconstruct the temperatures and age of the dolomitization waters within the Shakopee, Everton and St. Peter (Fig. 22). Land's (1985) equations for oxygen-isotope fractionation in dolomite-water systems were applied to the ∂^{18}O values from the dolomites within the Shakopee and Everton to complete the reconstruction. Results imply that D1 and D2 cements (Fig. 17) may have precipitated in Late Ordovician to Early Silurian at temperatures of 45° to 50°C, while the cement and dolomite replacement events (D3, RD1, RD2, RD3) may have occurred during the Late Pennsylvanian to Early Permian at temperatures of 90° to 95°C (Fig. 23). Due to the isotopic results of the D3, RD1, RD2, and RD3 cements, and their overlapping variability, it is likely that the dolomitizing fluids did not lose as much heat as Bethke and Marshak's (1990) model suggested that they would.

Porosity, Permeability and Modeling

The multiple events of paragenesis observed in the Shakopee, Everton and St. Peter lithologies (Fig. 17) have been controlled by the complex interplay of several factors. These factors include: 1) original sedimentary facies, mineralogy and depositional fabric of these formations; 2) timing, composition, and hydrology of diagenetic water migration within the Illinois Basin; 3) extent of diagenetic water-rock interaction and resulting porosity and permeability evolution; and 4) Illinois Basin regional tectonics, burial history, and associated geothermal gradients (i.e. Moore et al. 1989; Choquette and James 1987). These factors resulted in the nearly 100% diagenetic alteration of D1 and D2 dolomite cements by RD1 replacement dolomite. D3 cement was then formed, followed by the partial replacement of both RD1 and D3 by replacement dolomites RD2 and RD3. This type of successive alternation of dolomite precipitation and replacement is common in many subsurface settings, where early-formed dolomites are diagenetically transformed into more highly crystalline dolomite later on that is thermodynamically more stable. This diagenetic series creates distinct trace element and isotopic composition alterations during water-rock interaction that reflect dolomite stabilization by basinal fluids at elevated temperatures (Cander 1988, 1994; Montañez and Read 1992; Whitaker 2010).

These conclusions that both water-rock interactions and fluid mixing caused dolomitization of the Knox Supergroup and Ancell Group lithologies are consistent with previous reconstructions of the origin and hydrology of brines within Paleozoic strata of the Illinois Basin. Hydrologic modeling suggests that the gravity-driven flow of meteoric water deep into the Illinois Basin, (which resulted from Late Paleozoic uplift and unroofing of the Pascola Arch), caused northward basinal brine migration and deposition of Mississippi Valley Type (MVT) ore deposits (Bethke 1986; Bethke and Marshak 1990, Marshak and Paulsen 1998). Integrated elemental and isotopic analyses of brines housed within early Paleozoic sedimentary rocks of the Illinois Basin indicate that they were formed from fluids derived from three different sources. These include (Leibold 1991; Stueber and Walter 1991): (1) the syn-depositional subaerial evaporation of seawater, wherein the extent of evaporation fell short of halite precipitation (based on chloride, bromide, and deuterium- and oxygen-isotope relationships); (2) moderate extents of water-rock interaction with subsurface shales, clays and events of limestone dolomitization (based on Ca, Mg, K, Na and $^{87}Sr/^{86}Sr$); and (3) mixing of the original evaporated seawater brines with as much as 50% meteoric water (based on deuterium- and oxygen-isotope covarations).

Evaluation of Illinois Basin Paragenesis and Cement Volume

Although all paragenetic events (Fig. 17) occur in all three formations throughout the study transect, the extent and resulting volumetric precipitation of the dolomitization events range from ~10% on the shelf to as much as 99% in the basin. Two separate hypothesis are considered here. One explanation for these diagenetic trends is that basinal brine migration became increasingly stratigraphically controlled by the contact of the St. Peter. As the deep subsurface burial waters migrated northward, the contact below the St. Peter became more impermeable due to a better developed basal shale. This hydrologic barrier might have been effective enough to significantly reduce the magnitude of subsurface water passing through and reacting with the St. Peter. The second possible explanation is that the later dolomitization events could have been related to subsurface hydrothermal water migration from the south. If accurate, these hydrothermal waters would have cooled with northward migration, lowering the reaction rates of dolomitization.

Bethke and Marshak (1990) propose that higher temperatures subsurface water altered the Knox and Ancell Groups. Their modeling suggests that warm saline groundwater migrated across the North American craton from the forelands of tectonic belts and left diagenetic signatures. Their evidence for brine migration was five-fold. (A) Ore bodies deposited from metal-bearing brines (B) Thermal histories anomalous with shallowly buried sediments (C) Regional potassium metasomatism (D) Epigenetic dolomite cements in ore bodies and deep aquifers (E) Correlations of petroleum to distant source rocks. However, not all features observed in this study can be explained by Bethke and Marshak's (1990) model. While the highly altered and dissolved quartz, lack of calcite, and significant dolomitization observed in the present study are generally consistent, their model does not readily explain the lack of ore deposits and potassium metasomatism, as well as the abundance of anhydrite precipitates. The lack of ore deposits and potassium metasomatism could have been caused by the fluids moving in different horizons, as proposed by Marins (2007).

The primary physical evidence in the present study for late high-temperature (>90°C) structurally controlled hydrothermal alteration are brecciation and normal faulting, as seen in hand sample (Phillips 1972). Davies and Smith (2006) found that not only does structurally controlled hydrothermal alteration occur in conjunction with brecciation and faulting, but also with micro-fractures, vugs, and saddle dolomites. Fault conduits filled with internal dolomite sediment (Eichhubl and Boles 2000) are also caused by hydrothermal activity. These features are observed in both the Shakopee to a small extent, and ubiquitously in the Everton.

Depletion of heavier ^{18}O isotope in the Shakopee and Everton found in this study could be attributed to thermal fractionation. Brannon et al. (1992) and Christensen et al. (1996) support the timing of the hydrothermal brine migration to occur during the early Permian that could account for this depletion. Some trace pyrite and a later dolomite (D4) found in this investigation further support a later hydrothermal dolomite event. Comparison of isotopic distributions of dolomites precipitated in different environments (Badiozamani 1972) with data collected in this study find that the Shakopee and Everton isotopic values overlap with those of hydrothermal fields.

Marino (2007) found strong evidence supporting hydrothermal brine migration using vitreous reflection that paleotemperatures decrease from the southern Illinois Basin to the north, implying a transient heat source in the south. Due to irregularities in the south from normal faulting and fractures, there is no correlation between depth and paleotemperature. He found that there were more permeability horizons in the broken up rocks at the southern end of the basin, and, further north, the fluids were focused along a younger Mississippian unconformity . The only hydrological model compatible to the paleogeotherms is one in which hot fluid flowed through multiple horizons linked by permeable fault zones where temperature could not be stratigraphically controlled. This could explain the volumetric discrepancy of dolomite cements through the basin north-to-south transect. If paleotemperature did not correlate to depth, the temperatures in the north could have been more similar to the temperatures in the southern deeper portion of the basin than initially anticipated, and could explain the same type of cements and signatures of the events. It is possible that the difference in cement volume is then related to the decrease in saturation of the dolomitizing ions in the basin fluid waters.

Whitaker's (2010) reactive transport model, (which also supports the strange volume of anhydrite) shows that geothermal convection of normal seawater can form massive dolomites within one to tens of millions of years, which are also accompanied by precipitation of anhydrite downstream. This possible explanation for the trend of increasing anhydrite in the southern end of the basin has some merit, especially considering the extent of anhydrite present. However, typically halite usually is present with gypsum and/or anhydrite in such environments. Leibold et al. (1991) explained the absence of halite through elemental and isotopic analysis of early Paleozoic Illinois Basin fluid inclusions and found that evaporation fell short of halite precipitation, explaining its absence.

Stueber and Walter (1991) suggest that during Silurian-Devonian time, subaerially evaporated, penesaline brine entered the subsurface where it interacted with the rock. Results indicated that Na and K were depleted due to interaction with clay minerals, Ca was enriched, Mg was depleted by dolomitization, and Sr became enriched as a result of $CaCO_3$ recrystallization and dolomitization. They suggest that although the brine waters were significantly diluted by meteoric waters, the original marine bring waters were not completely expelled. The $^{87}Sr/^{86}Sr$ ratios suggest a two-component mixing trend, likely caused by petroleum migration from New Albany shales into the lower carbonates where it mixed with remnant evaporated seawater. This event probably preceded the influx of meteoric water because the $\partial^{18}O$ doesn't correlate with the Sr isotopic compositions of the formation waters.

Radiometric ages of K-bearing minerals indicate a later Pennsylvanian and Permian alteration. Other studies (Badiozamani 1972, Pitman and Spoeetl 1996, Cander 1988, Odom 1979 and Montañez 1994) have found that $^{87}Sr/^{86}Sr$ isotopic compositions of saddle dolomite from the Lower Ordovician Knox Group (Montañez 1994) matches up with the isotopic compositions of this study, proposing a radiogenic isotope enrichment of strontium. The most likely sources for this radiogenic Sr in the Illinois Basin are early Paleozoic shales such as the New Albany Shale or the crystalline Precambrian Eastern Granite Rhyolite Province basement (Kolata and Nimz 2010).

CONCLUSIONS

This study used paleobathymetric correlation of the sedimentology, stratigraphy, paragenesis and geochemistry to analyze formations within the Illinois Basin. The Ordovician aged Shakopee Dolomite, Everton Formation and St. Peter Sandstone, were analyzed for diagenetic events, porosity occlusion, and dissolution as well as fracturing. Results indicate that subsurface dolomitization has dramatically reduced primary porosity, which is more pronounced in the underlying Shakopee and Everton, with porosity reduction increasing in overall extent toward the southern basin.

Three sample locations selected for this study were based on relative paleoceanographic position along a north-south transect through the Illinois Basin. The three locations included: (1) core from the shallow marine shelf in Stephenson County (UPH well); (2) hand samples from the LaFarge Quarry in LaSalle County; and (3) core from the deep marine basin in White County (Superior Well). Quartz arenites and quartz wackes of the St. Peter overlie the Shakopee at the erosional Sauk/Tippecanoe I sequence boundary in the northern Illinois Basin. The Shakopee is a fine-grained dolomite with thinly bedded shales and siltstones. In the southern deeper portions of the Illinois Basin, the St. Peter directly overlies the Everton, which is a near shore dolomitized marine deposit containing irregular lenses of quartz sands. The Everton is broken up into two members: (1) a lower white quartz arenite to quartz wacke member and (2) a upper dolomitized crystalline carbonate, mudstone and wackestone member. Biostratigraphic correlation of the Everton and overlying St. Peter suggests that the Everton is age conformable with both the Shakopee and the St. Peter in the basin. However, sedimentologic composition and diagenetic alteration patterns suggests that the Everton belongs within the Knox Supergroup instead of the Ancell Group. Besides defining the boundary between the Sauk and Tippecanoe I sequences, this contact acted as an increasingly efficient subsurface aquatard with movement toward the northern shelf and limited dolomitization within the St. Peter.

A suite of 61 polished thin sections were analyzed with detailed PL and CL petrography. An early quartz cement and two dolomite cements (D1 and D2), are separated from later dolomites by a major event of early shallow burial dissolution. Later deep burial diagenesis included precipitation of a pink-red CL dolomite (RD1) replaced the D1 and D2, which was followed by a third non-CL dolomite cement (D3) and a later diagenetic anhydrite precipitation. Two late replacement dolomites (RD2 and RD3), which exhibit dark red and yellow-orange CL respectively, replaced all of the prior dolomitization events. This sequence was capped by the precipitation of a late bright blue CL quartz cement. The early dolomite event was found to have occurred during the late Ordovician/early Silurian from 45-50°C while the late dolomitization occurred during the late Pennsylvanian to early Permian at temperatures around 90-95°C. Covariation modeling of $\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ imply that the dolomitizing fluids were derived from brines that have reacted with the basement Precambrian Eastern Granite Rhyolite province or the overlying New Albany shales. Although these diagenetic events have significantly reduced porosity locally, the Shakopee, Everton and St. Peter deposits have retained as much as 10 to 30% porosity on the northern shelf and therefore theoretically remain viable subsurface reservoirs for CO_2 sequestration and oil and gas entrapment. However, carbon sequestration in the deep southern portion of the basin is not a viable option at this time.

FIGURES

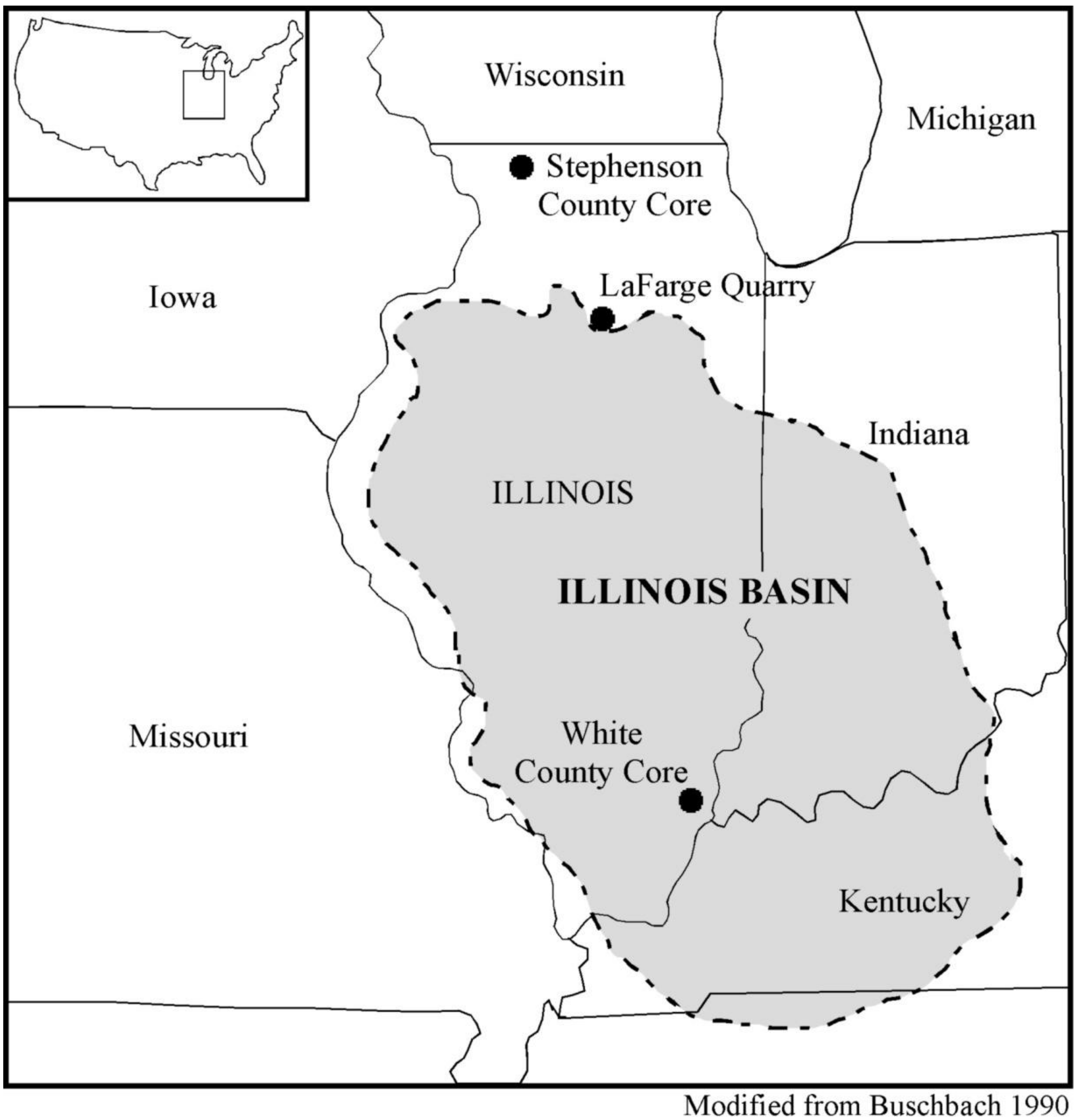
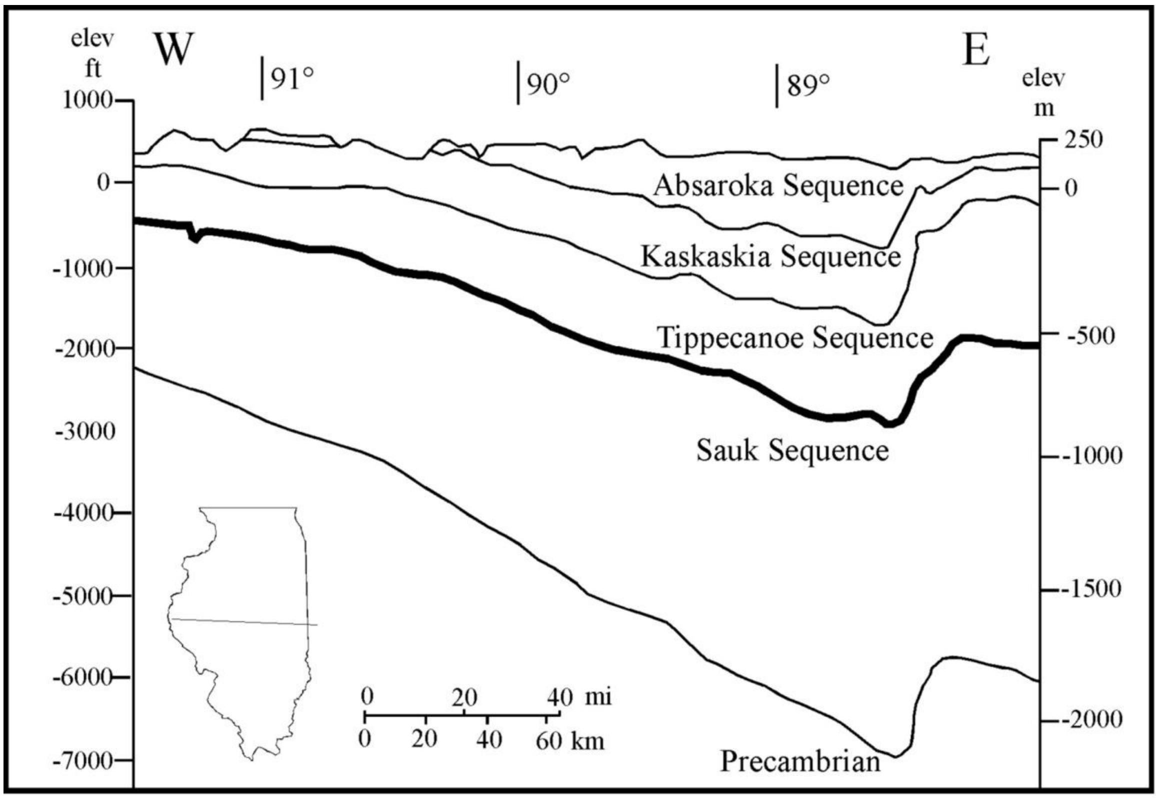


Figure 1. Geographic map of the Illinois Basin (after Buschbach 1990) showing the locations of the Stephenson County Core, LaSalle County Quarry and White County Core sample sites.



(modified from Kolata 1990)

Figure 2. East-West cross section of the Illinois Basin with sequence boundaries identified by Sloss 1963 (from Kolata 1990).

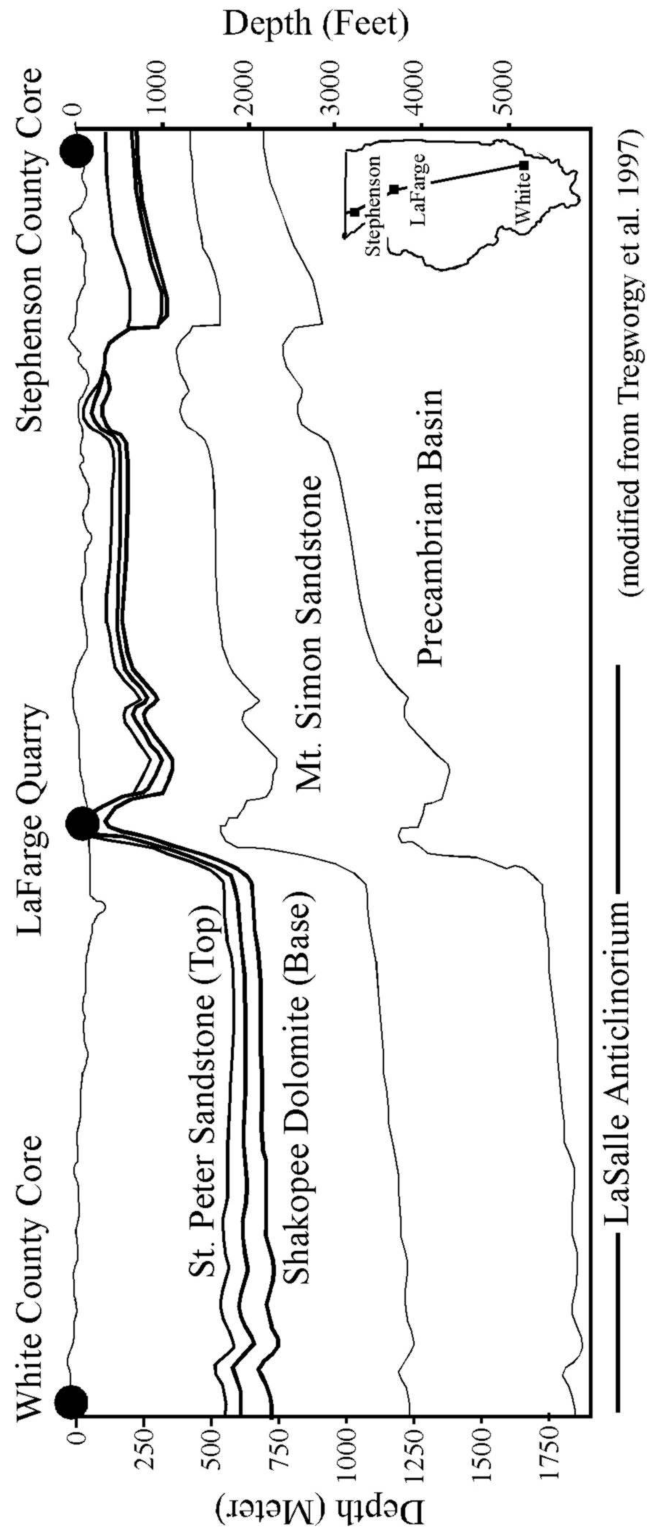


Figure 3. North-south oriented structural and stratigraphic cross-section of the St. Peter-Knox unconformity within the Illinois Basin (after Tregworgy et al. 1997) correlated through the Stephenson County Core, LaSalle County Quarry and White County Core sample locations.

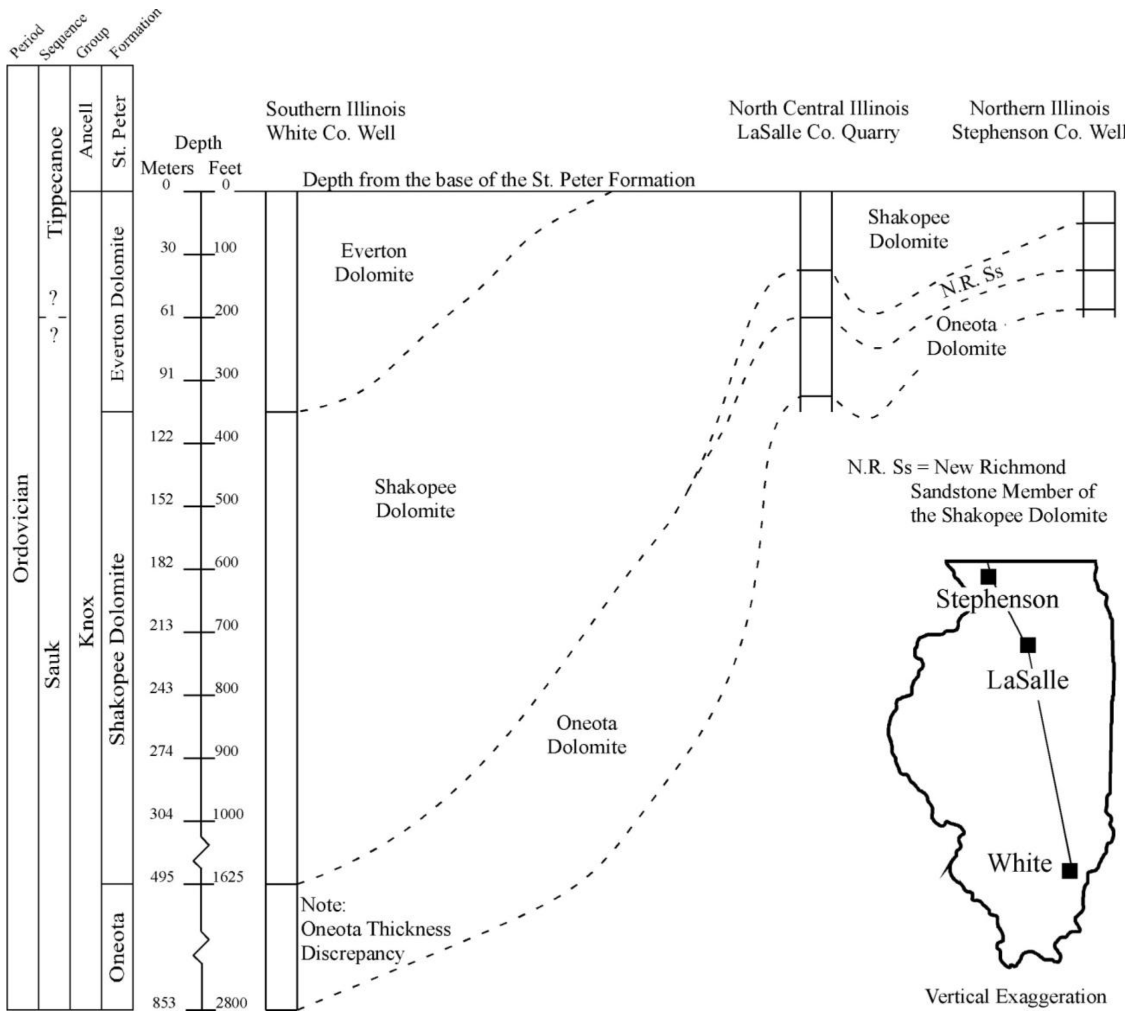


Figure 4. North-south stratigraphic cross-section and paleobathymetric reconstruction of the Knox Group formations within the Illinois Basin. Insert shows cross-section transect (data from Tregworgy et al. 1997).

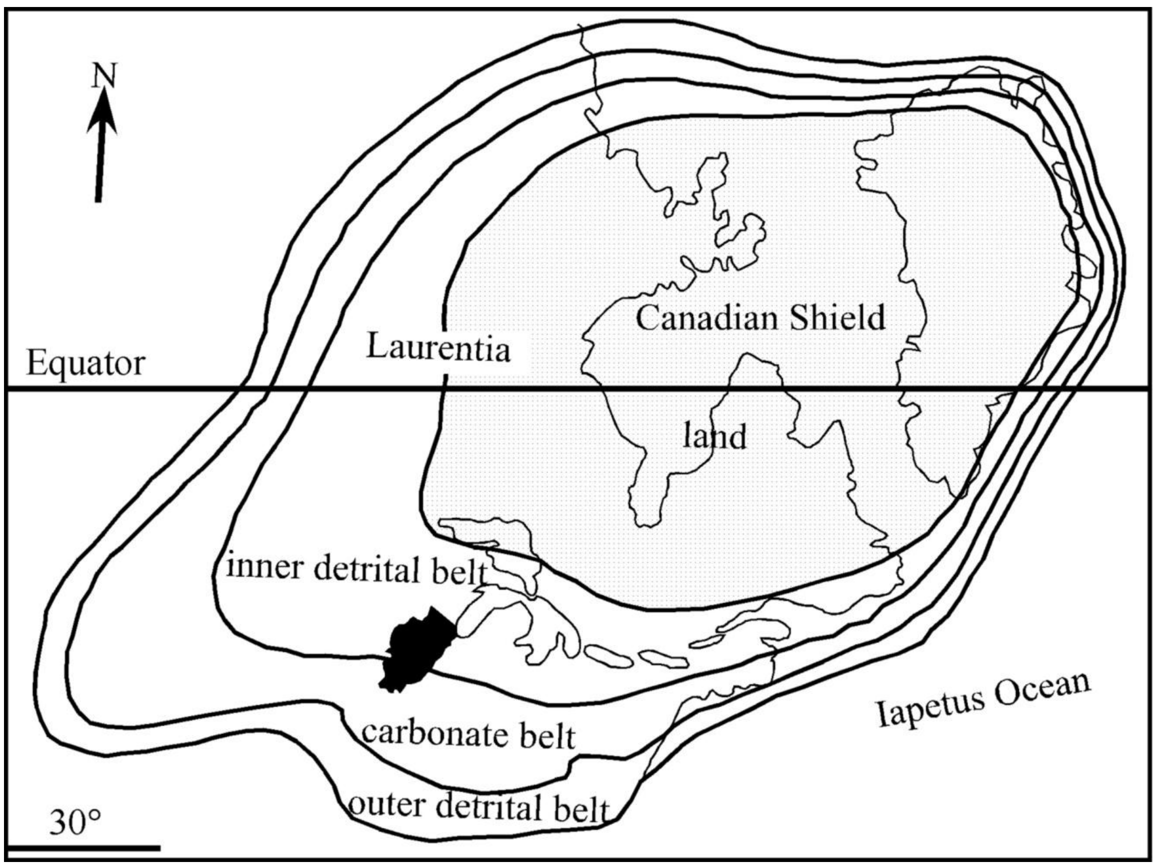


Figure 5. Illinois Basin paleooceanic schematic of Ordovician Sea Level (from Bushbach 1964).

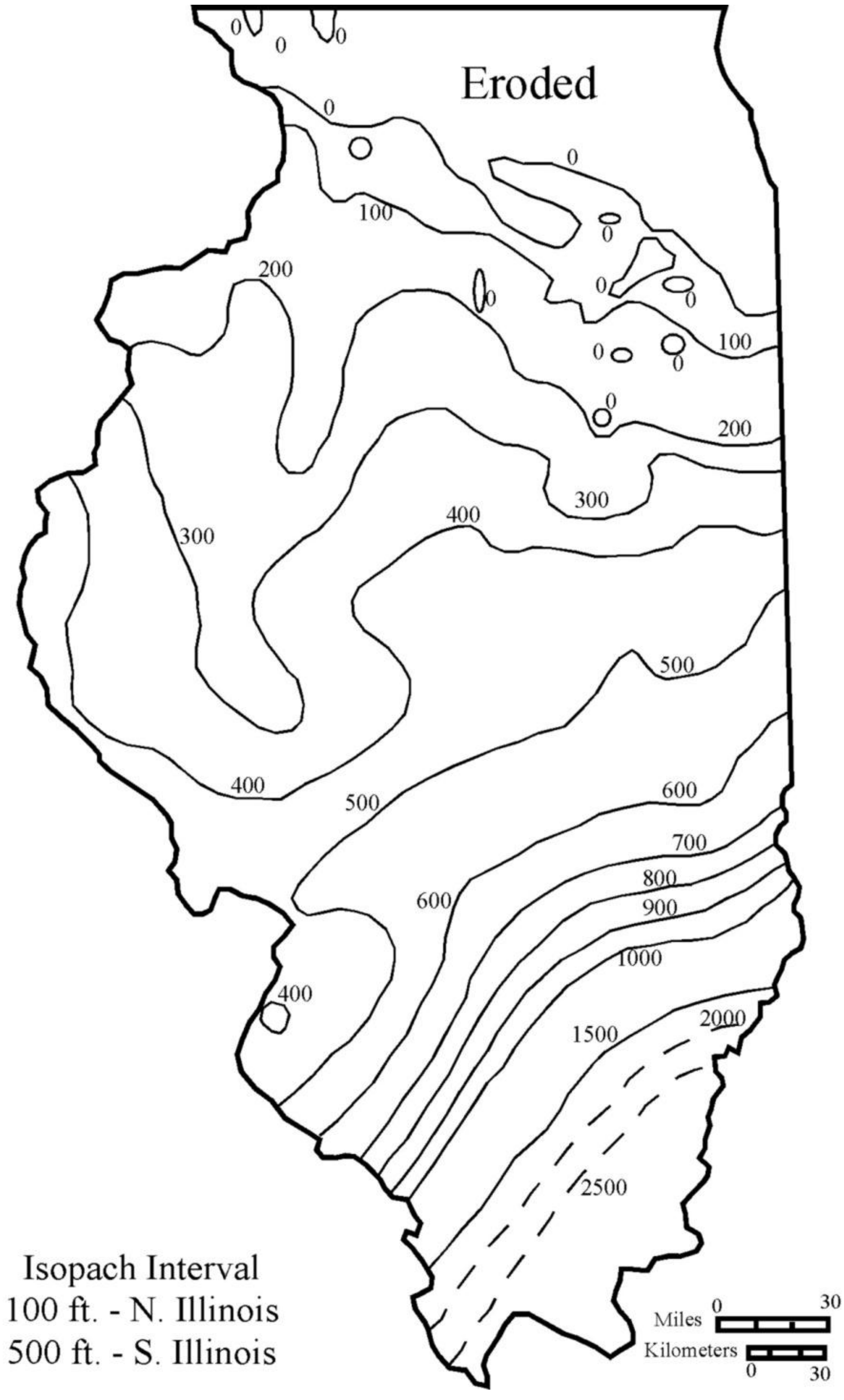


Figure 6. Shakopee isopach map (from Willman 1970).

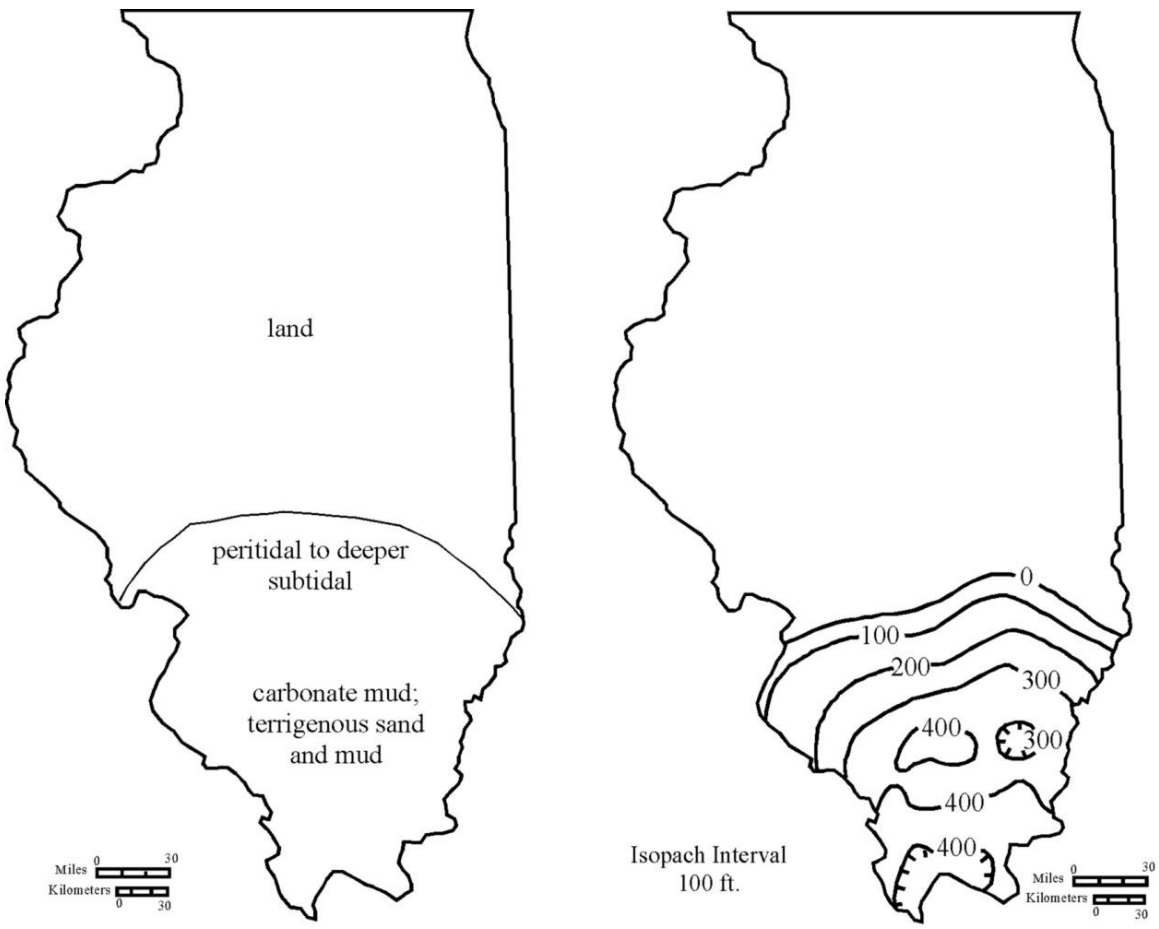


Figure 7. Everton isopach map and paleogeographic reconstruction of the Illinois Basin during Whiterockian time (from Kolata and Noger 1990).

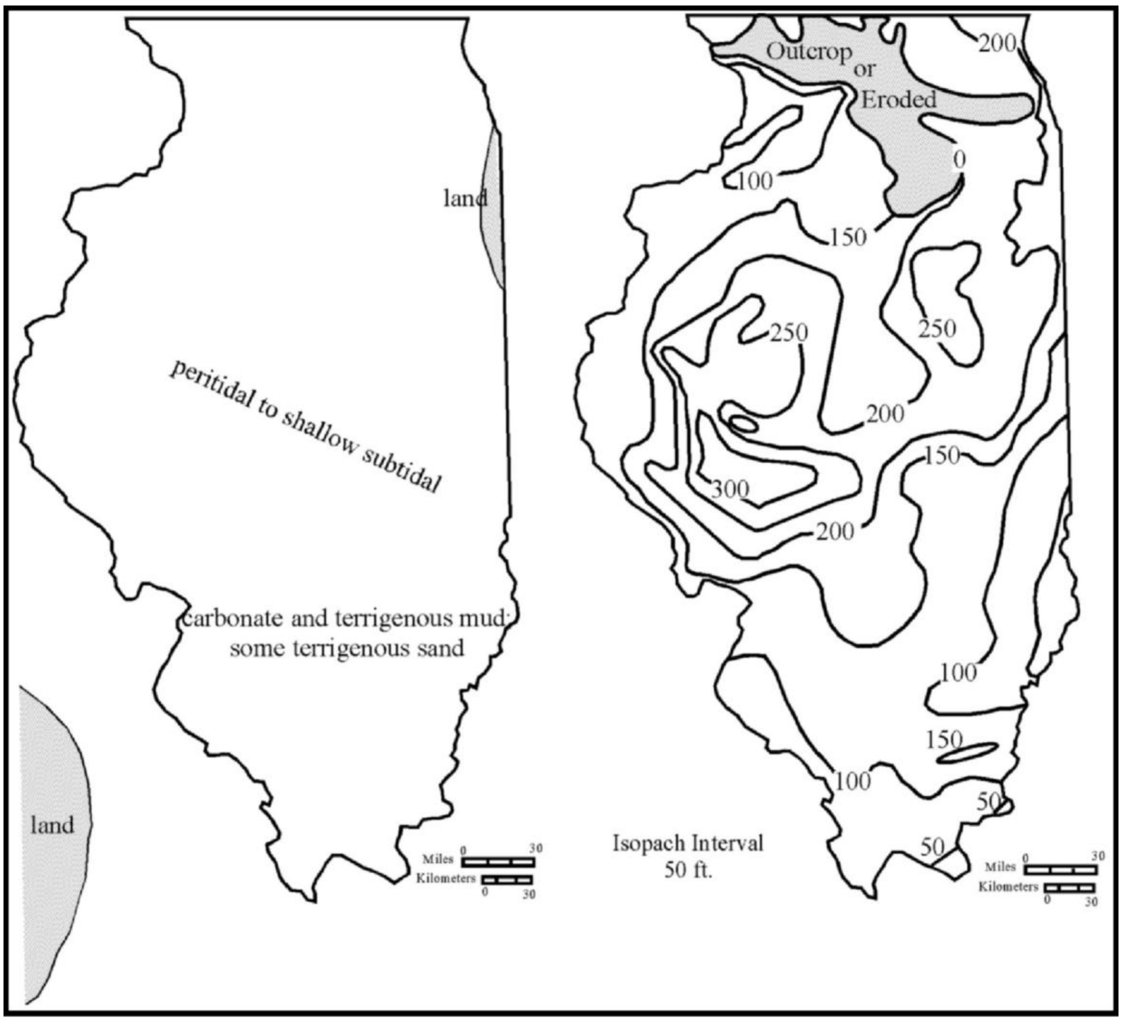


Figure 8. St. Peter isopach map and paleogeographic reconstruction of the Illinois Basin during Chazyan time: St. Peter deposition (from Kolata and Noger 1990).

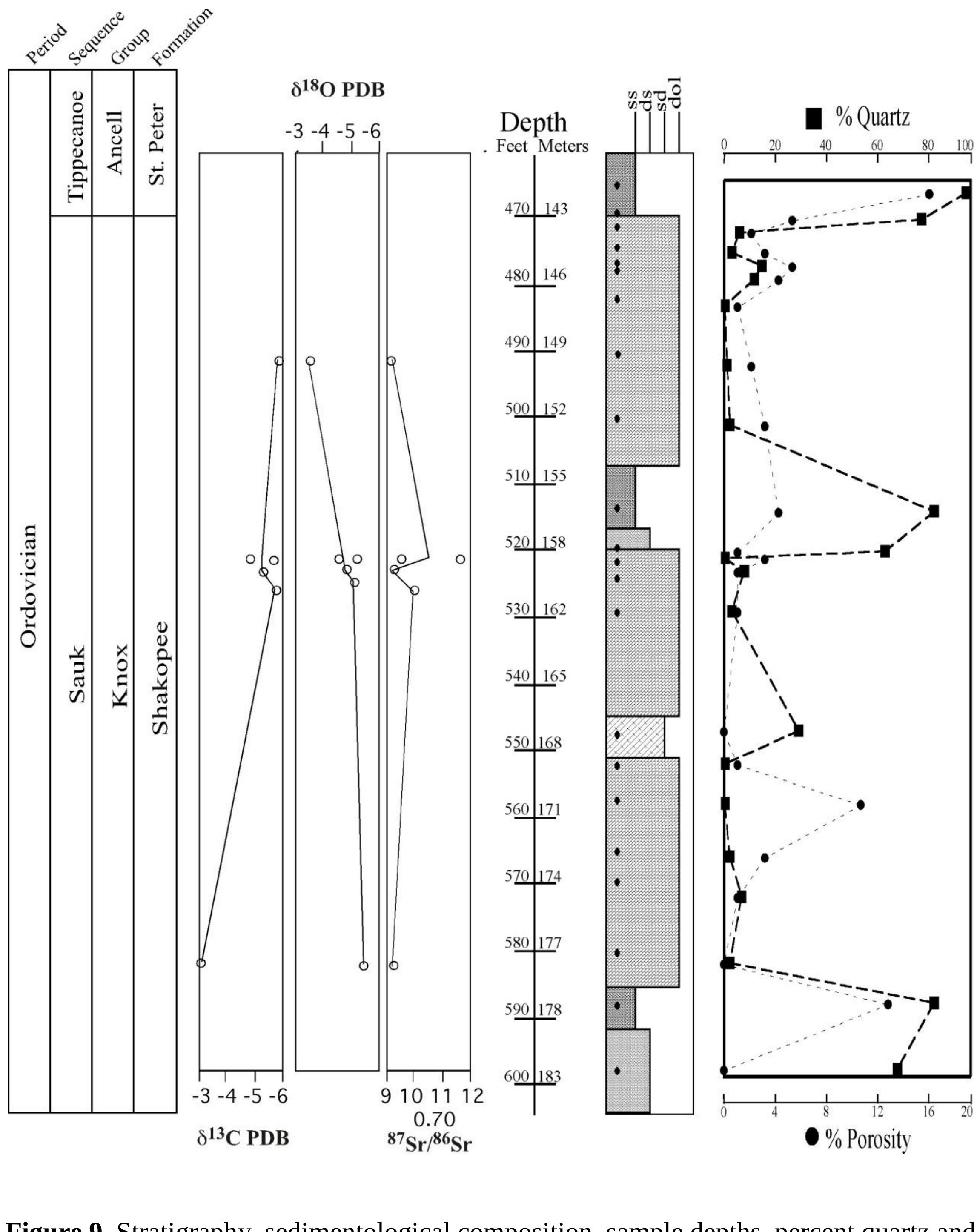


Figure 9. Stratigraphy, sedimentological composition, sample depths, percent quartz and porosity, and isotopic values of the Stephenson County Core (UPH well).

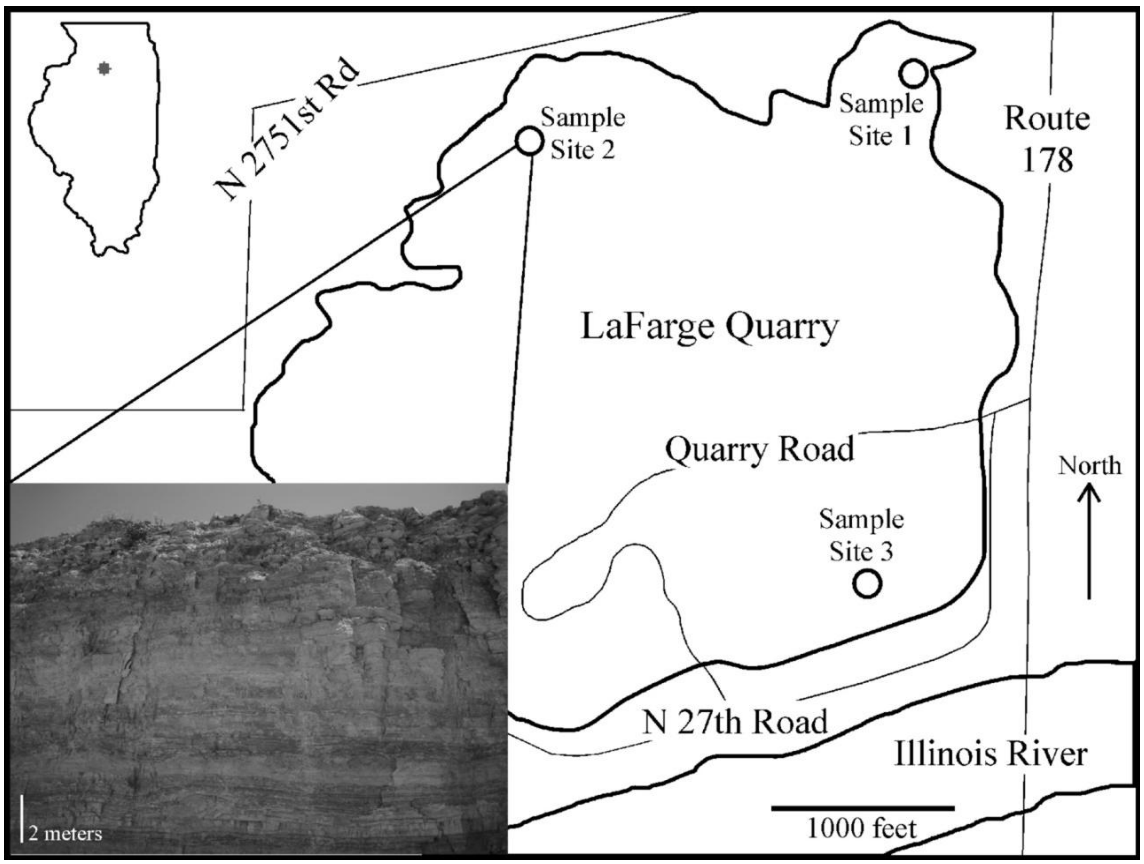


Figure 10. Geographic map and field photographs of sample sites at the LaFarge Quarry in LaSalle County, Illinois.

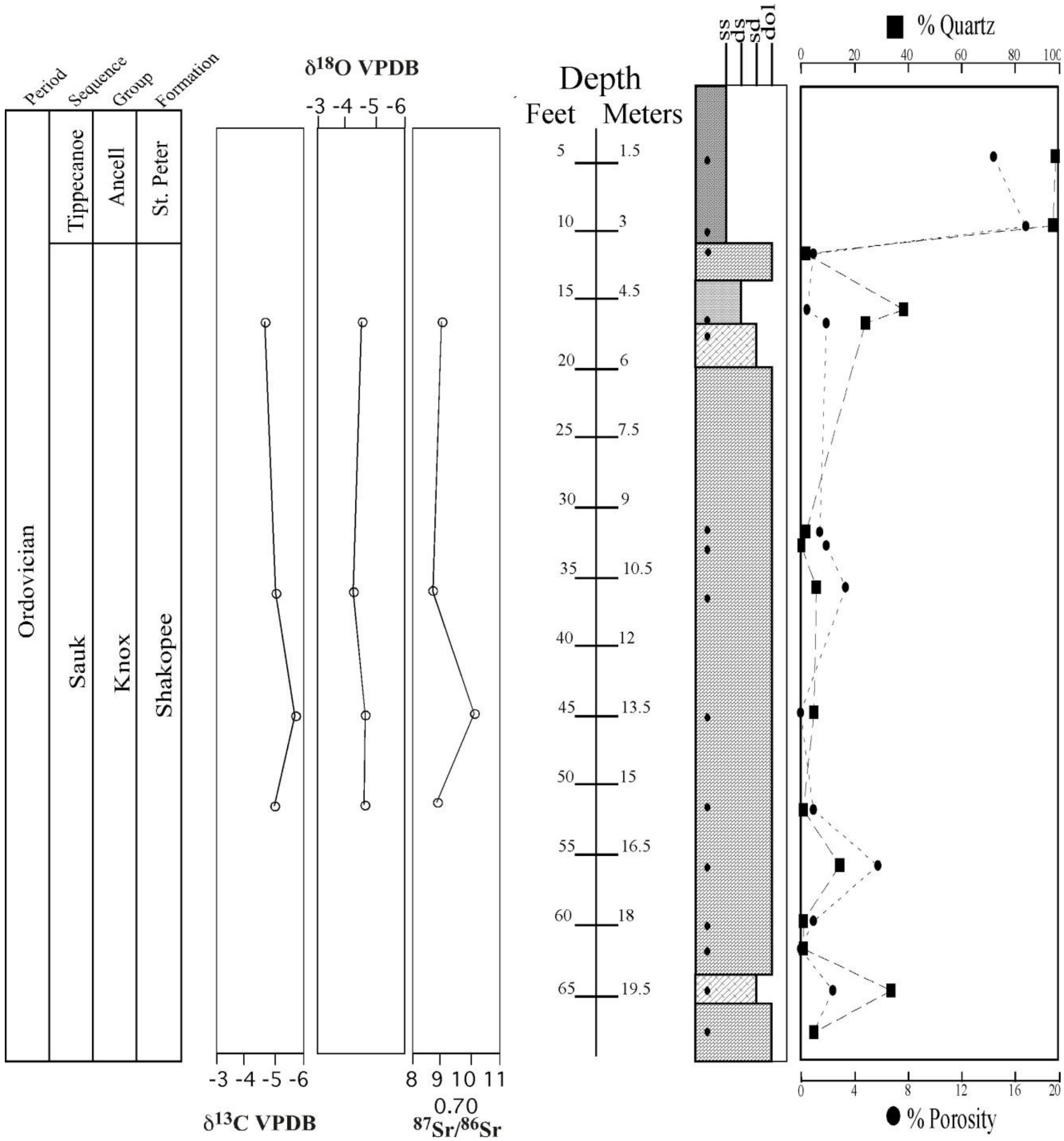


Figure 11. Stratigraphy, sedimentological composition, sample depths, percent quartz and porosity, and isotopic values of the LaFarge Quarry.

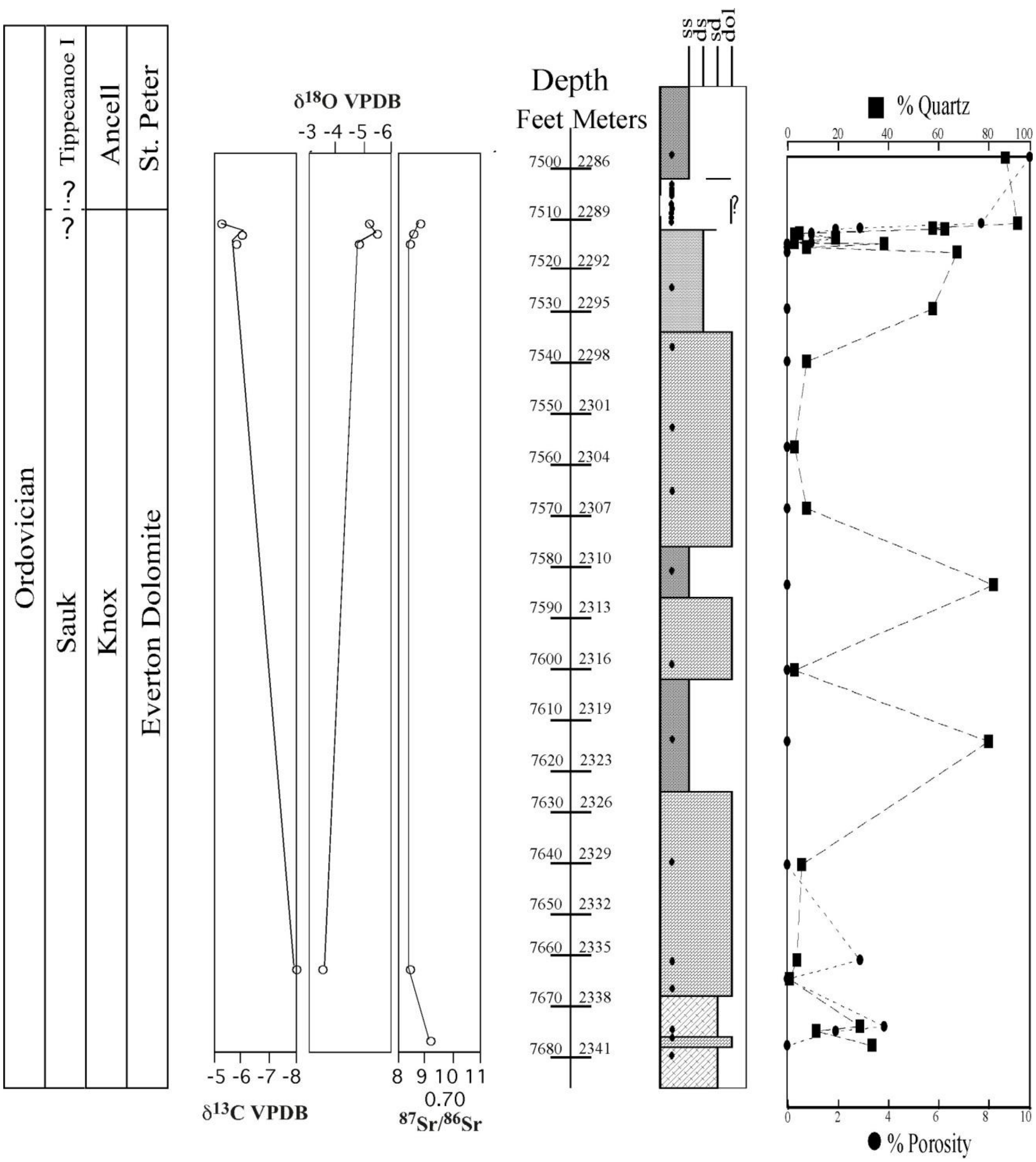


Figure 12. Stratigraphy, sedimentological composition, sample depths, percent quartz and porosity, and isotopic values of the White County Core (Superior Well).

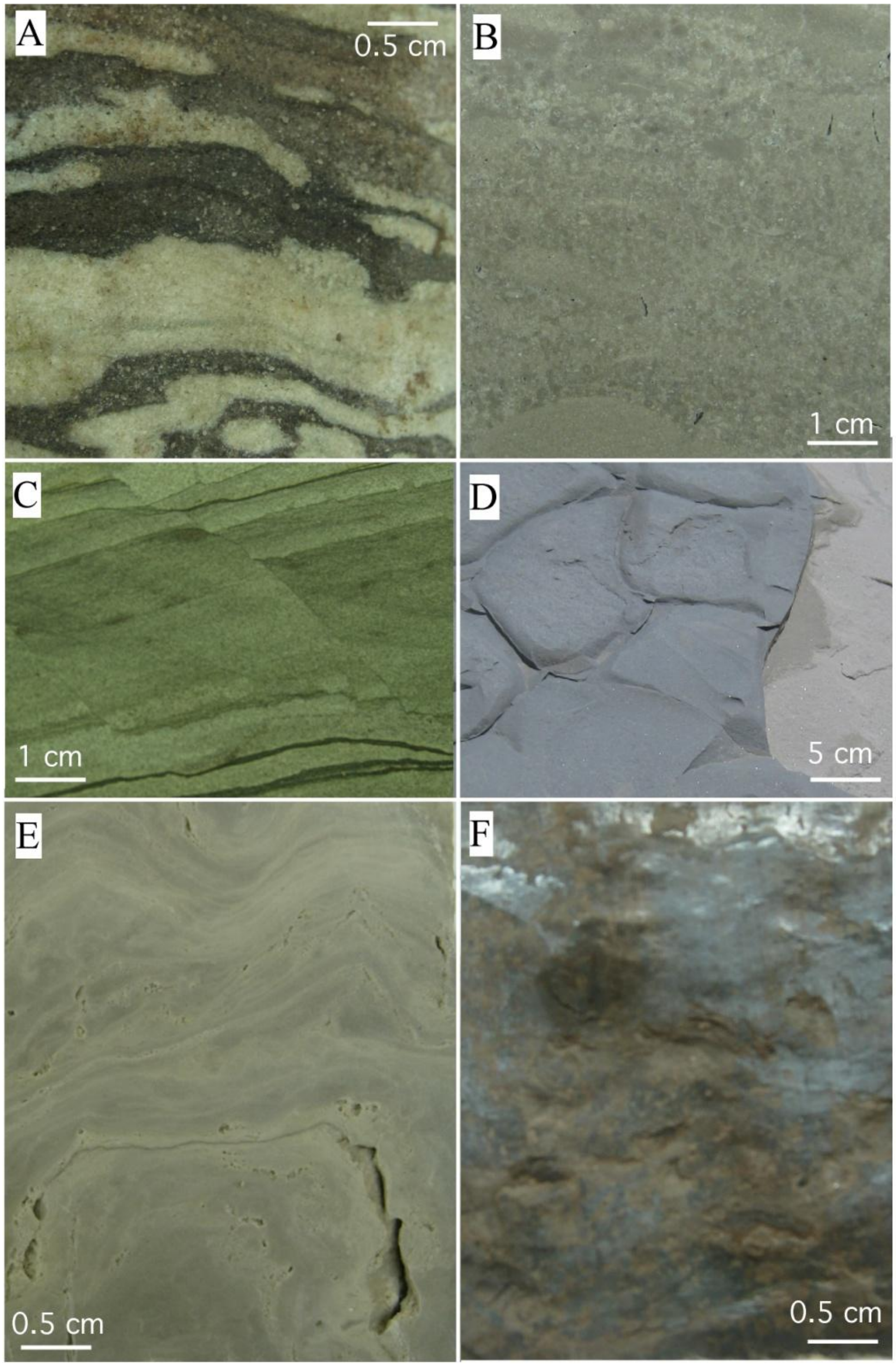


Figure 13. Shakopee Lithologies (A) Soft sediment deformation of argillaceous sandstone and sandy shale layers. (B) Rounded centimeter scale rounded lithoclasts. (C) Centimeter scale micro fractures and faults (D) Centimeter to decimeter scale mudcracks (E) A section of a stromatolite bed (F) Pseudo-horizontal bedding with slicken lines

Figure 14. The Sauk-TIppecanoe I Sequence Boundary (A) The sequence boundary between the lower Shakopee and overlying St. Peter in LaSalle County exhibiting fractures, fracture fill and erosional effects. (B1 and B2) The conformable gradational contact between the lower Everton and the overlying St. Peter in White County.

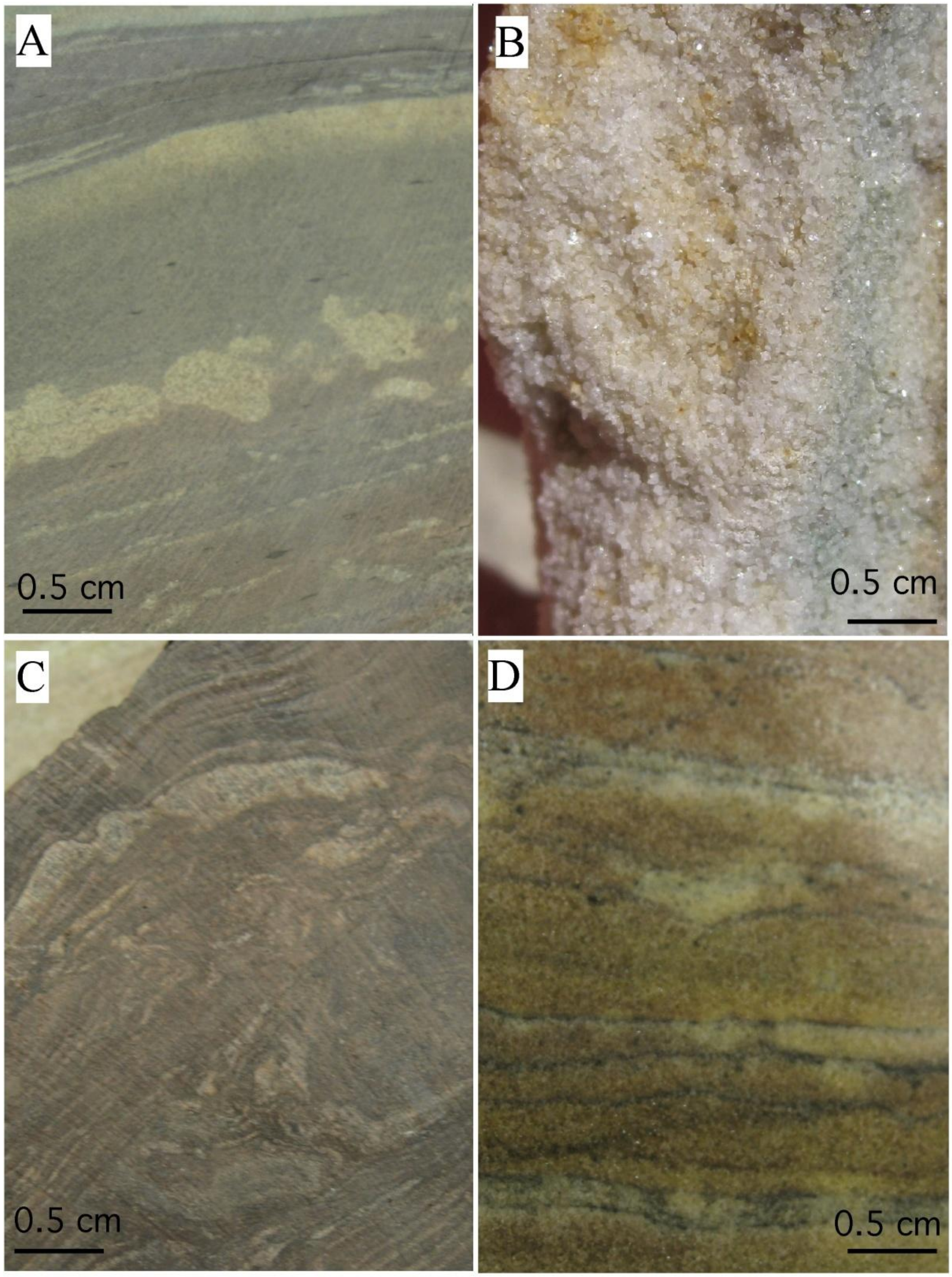


Figure 15. The St. Peter Lithologies (A) Basal St. Peter interbedded shale and sandstone layers (B) Pure typical massive bedding quartz arenite (C) Soft sediment deformation of the basal shale layer (D) Rare argillaceous millimeter scale sandstone layers interbedded with shale.

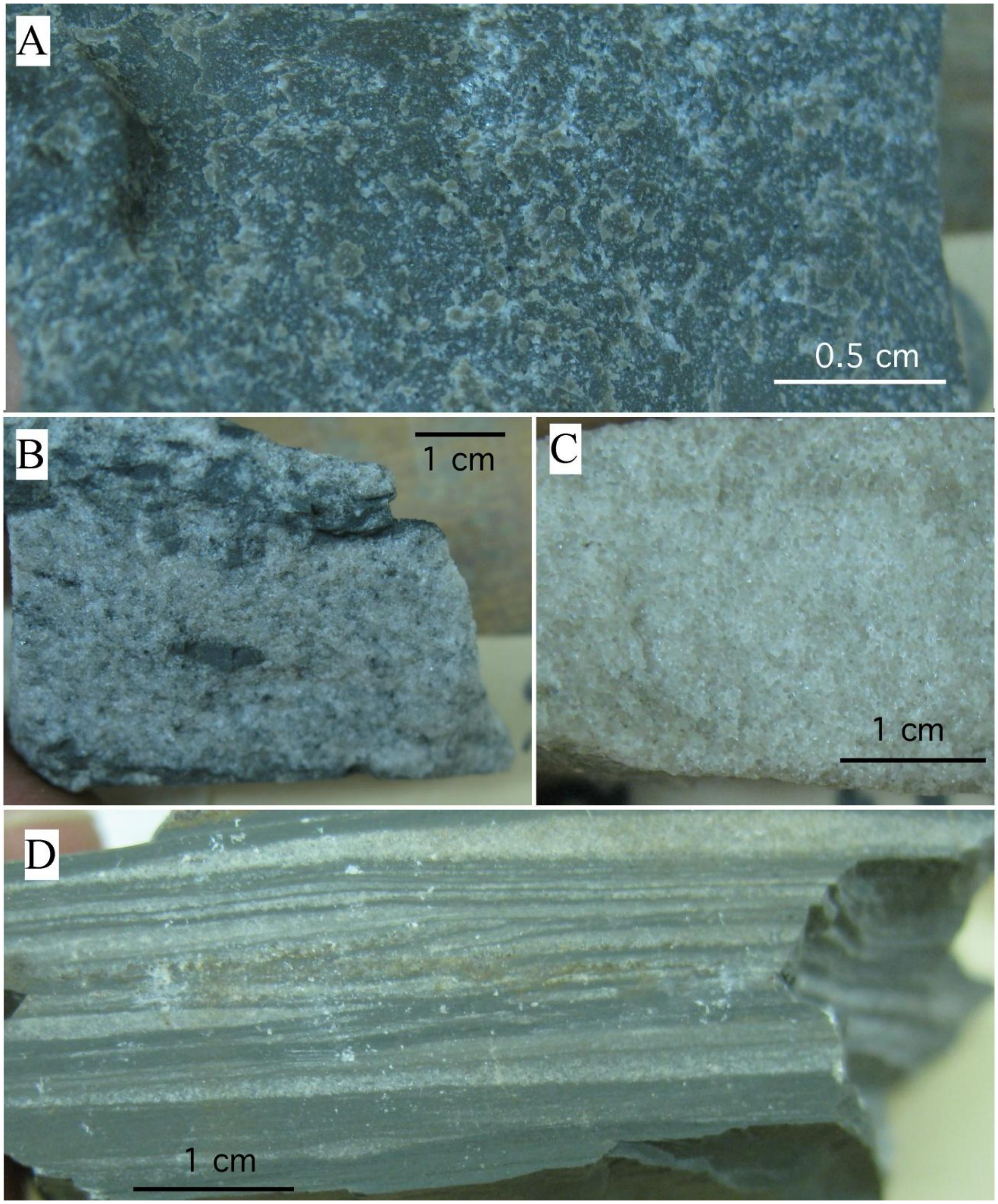


Figure 16. Everton Lithologies (A) Typical upper member dark gray dolomitic crystalline carbonate (B) Argillaceous dolomitic sandstone (C) Pure quartz arenite of the lower member (D) Millimeter scale beds of shale, dolomitic sandstone and dolomitic crystalline carbonate.

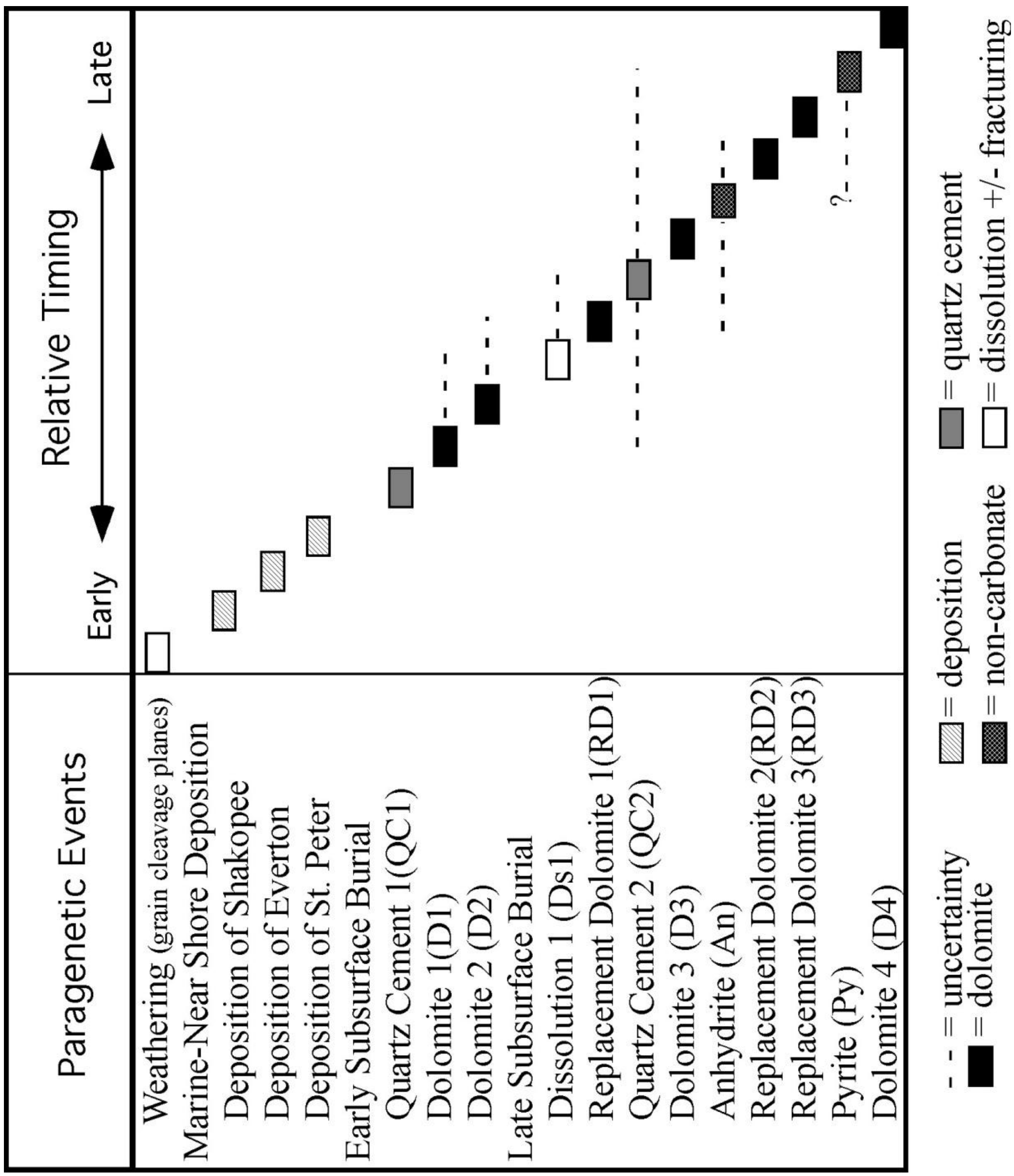


Figure 17. Combined paragenetic sequence of the St. Peter, Everton and Shakopee. The sedimentological and mineralogical composition of each event comprising the paragenetic sequence are presented in Table 1.

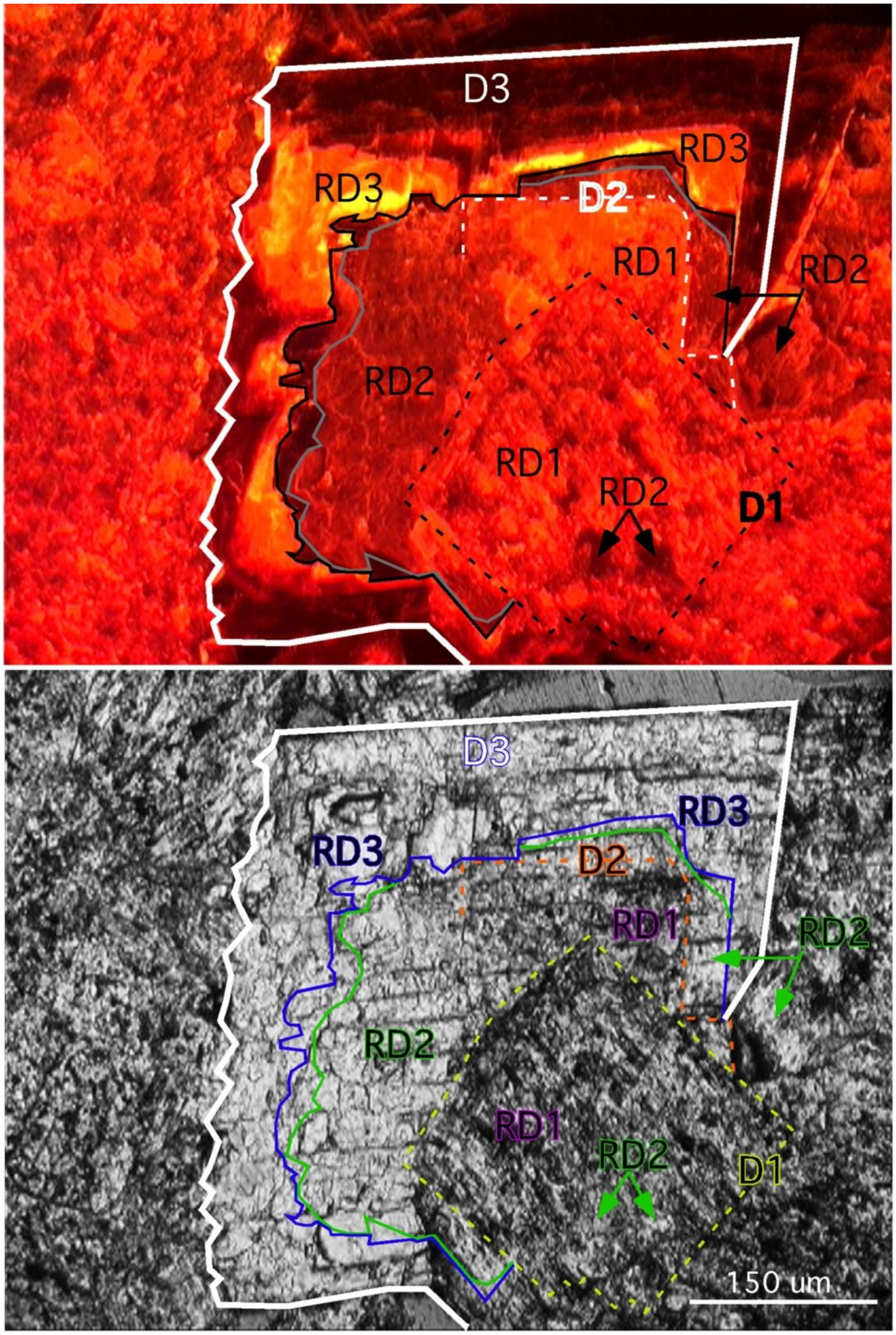


Figure 18. Paired plane-light and cathodoluminescence-light photomicrographs of sample 522 from the Stephenson County Core. The labeled paragenetic events refer to those presented in Fig. 13 and Table 1 and are described in the text. D1 is shown with D2 precipitated around it. Evidence for Ds2 is seen where a cloudy RD1 has replaced D1 and D2. A quenched D3 crystal has formed over D1 and D2. RD2 and RD3 have replaced previous dolomite events.

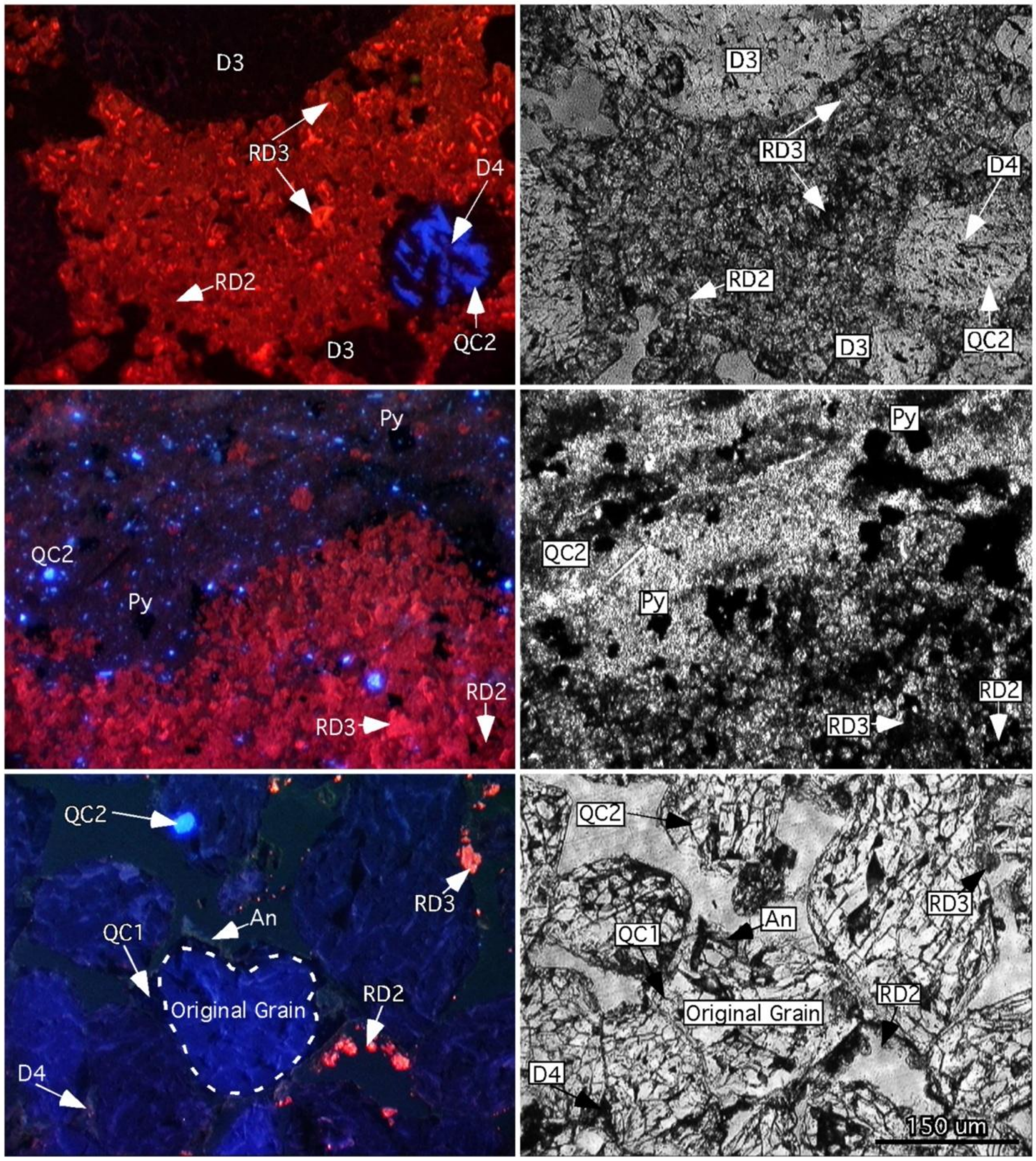


Figure 19. Paired plane-light and cathodoluminescence-light photomicrographs of samples from the LaFarge Quarry section. (A and B) D3 is replaced by RD2 and RD3. QC2 has precipitated through D3, RD2 and RD3. (C and D) A mix of QC2 and RD3 with trace pyrite make up the fine layer, where as RD2 and RD3 compose the medium grained layer. (EandF) The original quartz grains is fractured then the darker QC1 precipitated. Grain fracturing predominates even through the anhydrite cement. QC2 cuts through previously deposited minerals. RD2 and RD3 have formed on the crystal boundaries.

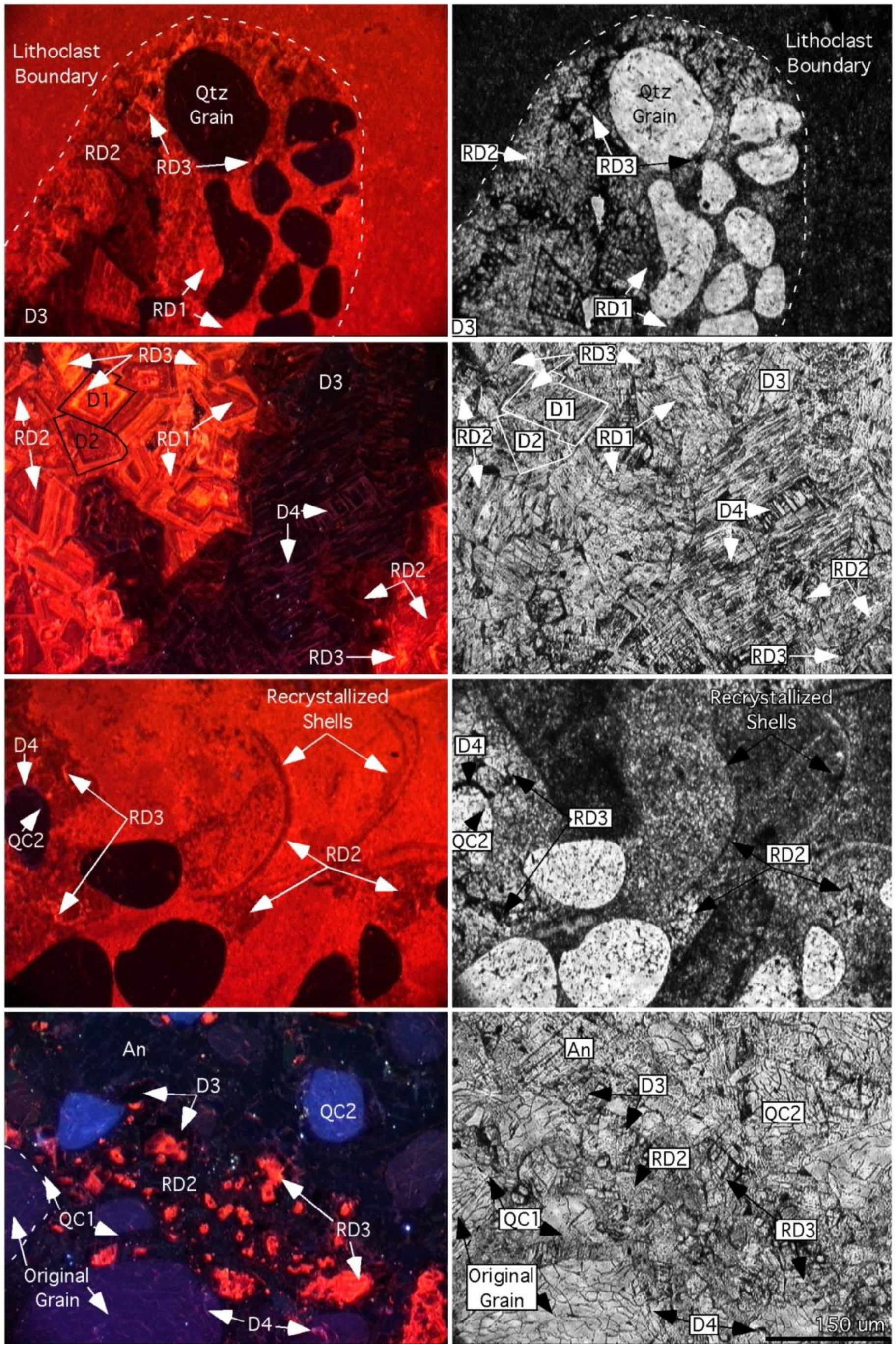


Figure 20. Paired plane-light and cathodoluminescence-light photomicrographs of samples from the White County Core. (AandB) Shown is a lithoclast within a wackestone that exhibits many late stage events including all three replacement dolomites. (CandD) Evolution of dolomitization events in order: D1, D2, D3, RD2, RD3 and D4 are highlighted. (EandF) Conodont shells are shown recrystallized by RD2 and RD3. (GandH) Fractured original grains with QC1 concentric overgrowths, D3 and anhydrite are visible, while anhydrite boundaries are ambiguous. Dolomite grains of RD2, RD3 and D3 can be seen as well as late QC2 and D4.

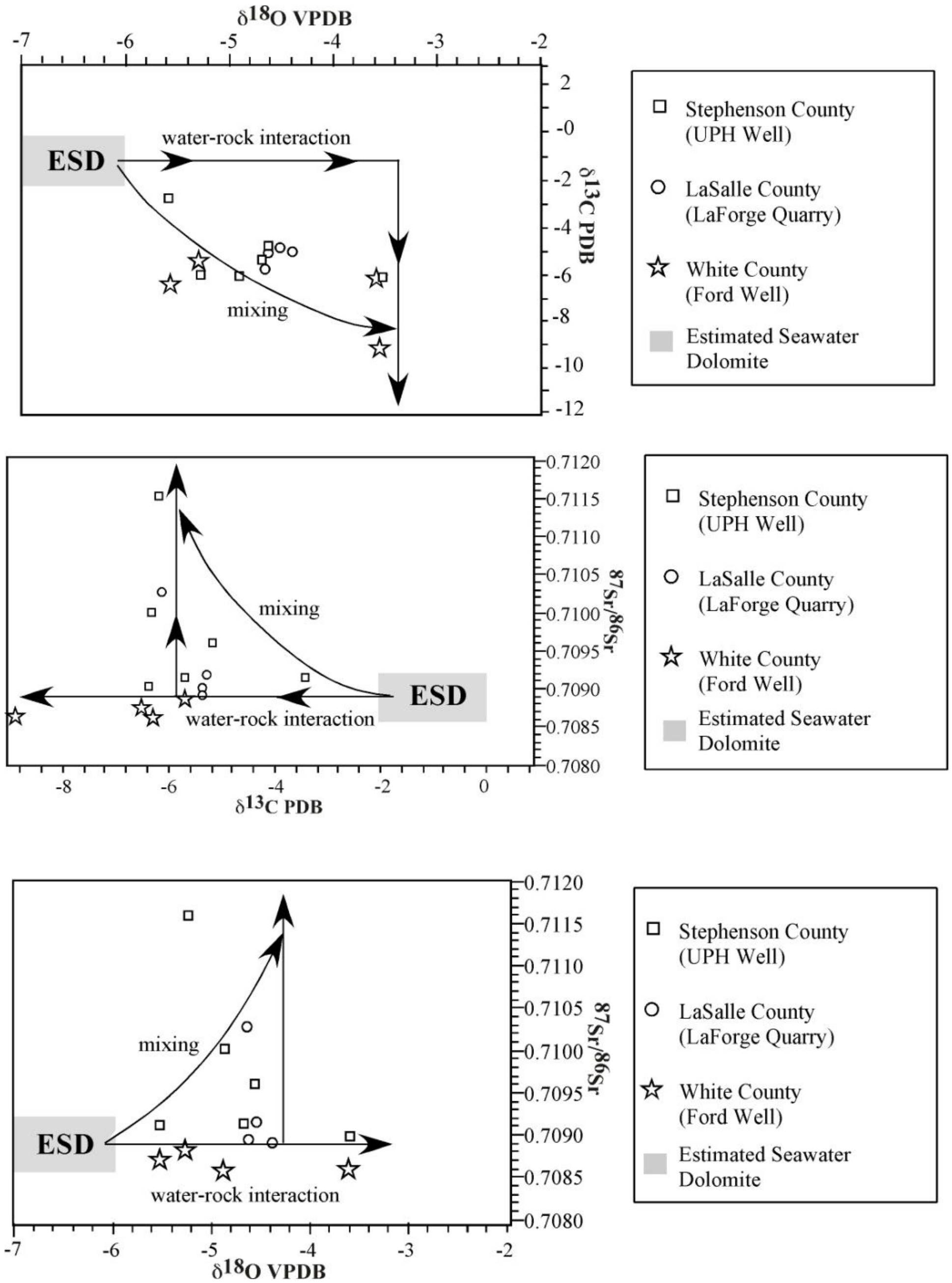


Figure 21. Geochemical cross-plots of microdrilled $^{87}Sr/^{86}Sr$, □^{13}C and □^{18}O compositions of dolomites comprising the St. Peter, Everton and Shakopee. Data are presented in Table 2. Iterative water–rock interaction trajectories for subsurface limestone dolomitization (water-rock interaction) are shown using mixing equations in Langmuir et al. (1978) and water–rock interaction equations in Banner and Hanson (1990). Binary mixing lines (Mixing) were calculated using equations in Faure (1986). The composition of an estimated sea-water dolomite (ESD) precipitated from Ordovician sea water was constructed from data in Veizer et al. (1999). Calcite–dolomite fractionation factors in Land (1985) were applied to estimate the ESD □^{18}O composition.

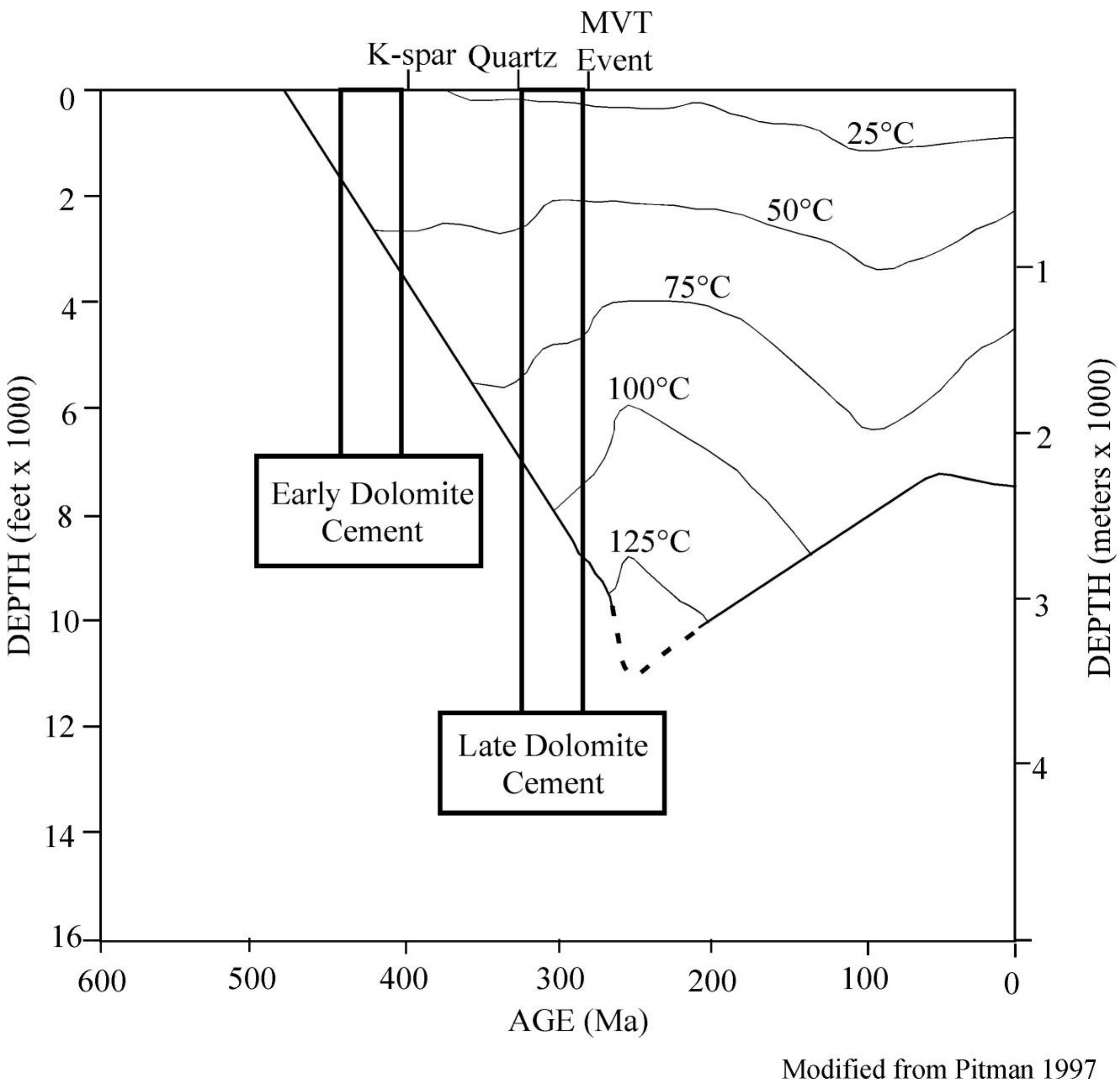


Figure 22. The burial curve and key paragenetic sequences from Pitman 1997 correlated with this study's Early Dolomite Cement and Late Dolomite Cement event to show depth, timing (absolute age) and approximate subsurface temperatures.

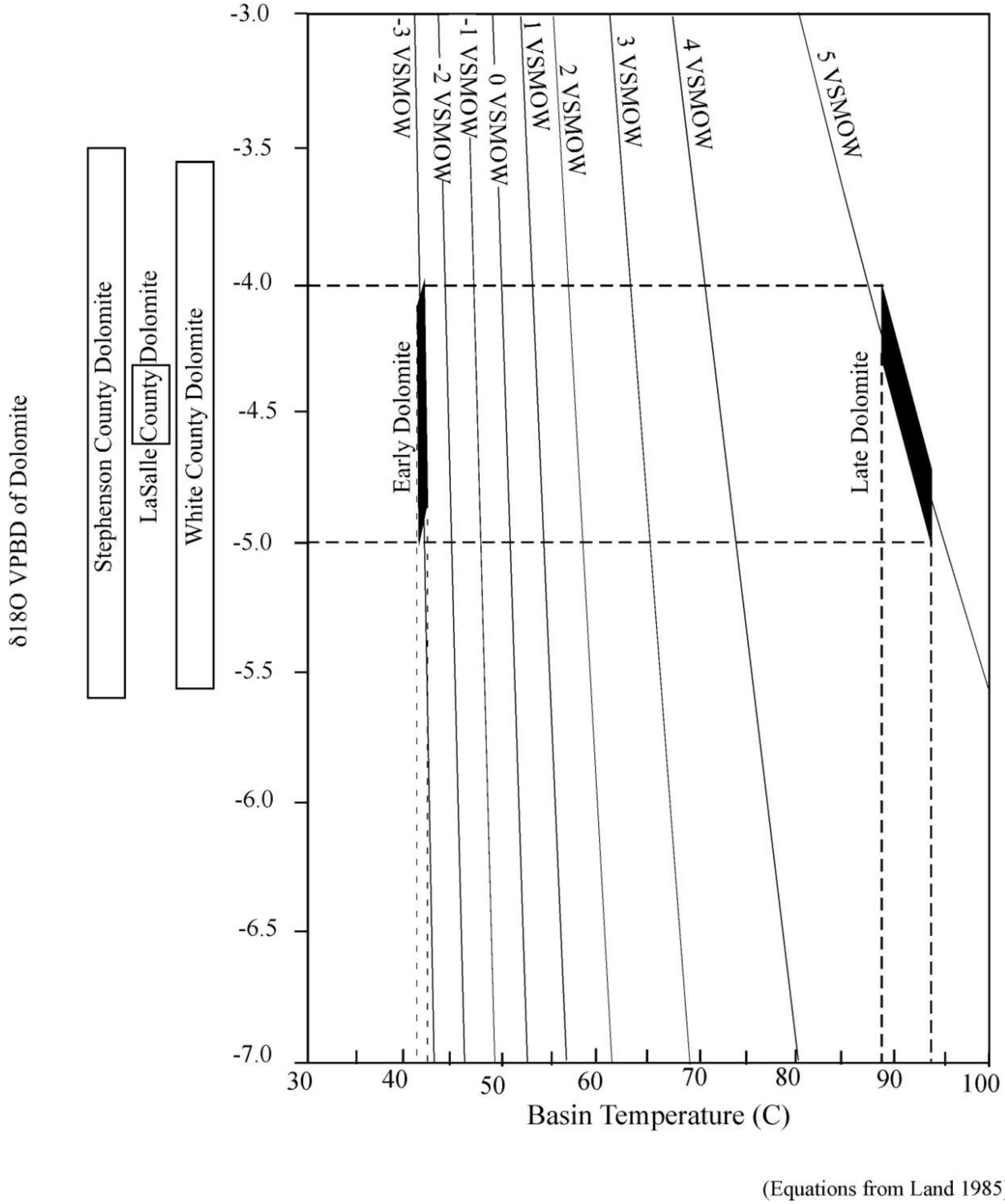


Figure 23. Cross plot of temperature vs. predicted d18O. Equations from Land 1985.

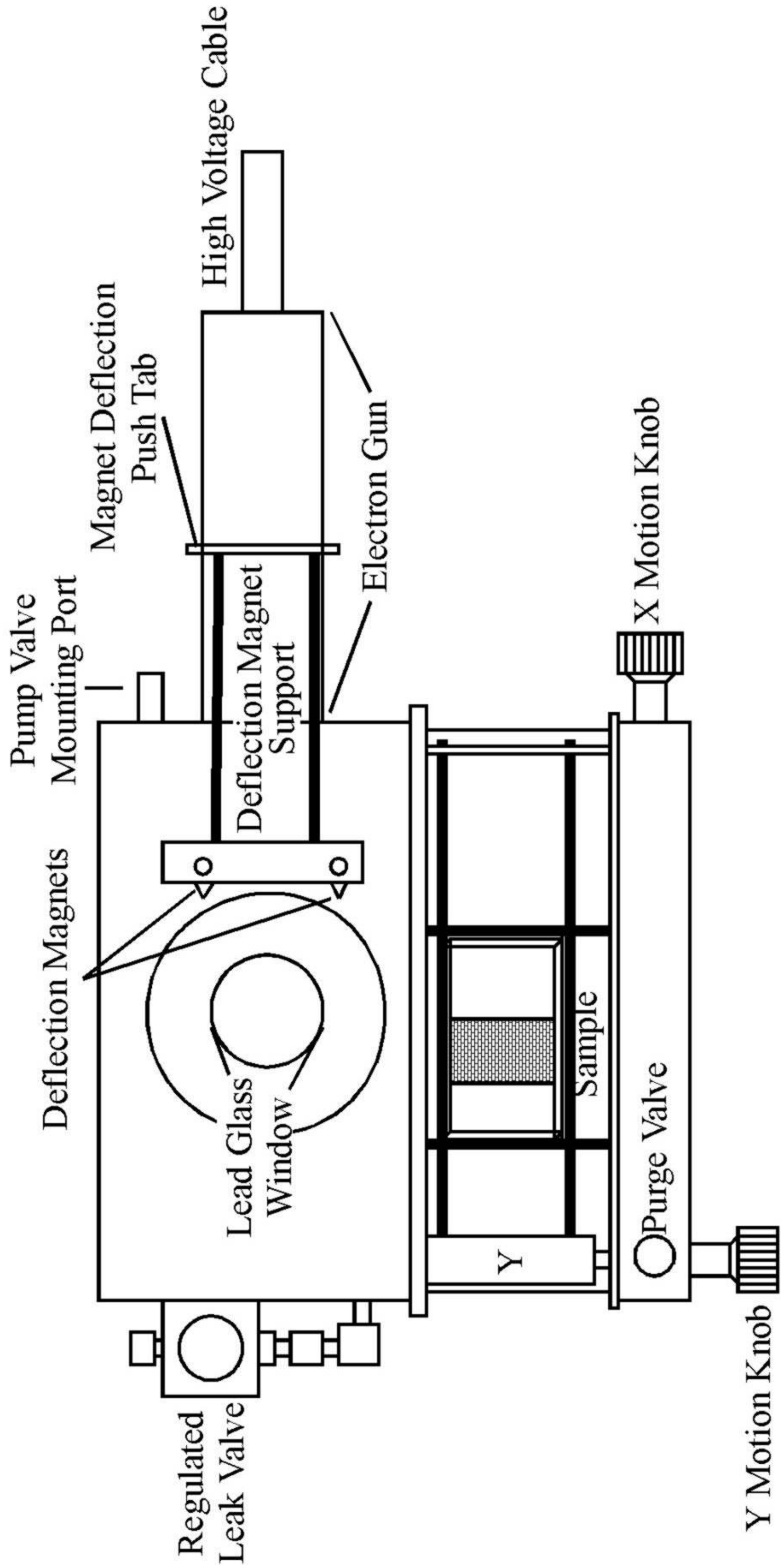


Figure 24. Fouke Lab Cathodoluminescent set up diagram (from Relion Industries 2010)

TABLES

Table 1. Description of the Minerals Observed in Thin Section

Paragenetic event	Crystal Morphology	Style of Precipitation	Crystal	Crystal Size (um)	Cathodoluminescence Color	Cathodoluminescence Zonations
Quartz Cement 1	Spheroidal	Cement	Euhedral	5-10	Dark Blue	Homogeneous
Dolomite 1	Rhombohedral	Cement	Euhedral	5-100	NA	...
Dolomite 2	Rhombohedral	Cement	Euhedral	10-30	NA	...
Replacement Dolomite 1	Rhombohedral	Replacement	Anhedral	1-5	Pink-Red	Mottled
Dolomite 3	Rhombohedral	Cement	Euhedral	5-50	Black	Concentric
Anhydrite	Orthorhombic	Recrystallization	Euhedral	5-125	Light Green	Mottled
Replacement Dolomite 2	Micritic	Replacement	Anhedral	1-5	Dark Red	Mottled
Replacement Dolomite 3	Various	Replacement	Anhedral	1-10	Yellow-Orange	Concentric
Pyrite	Cubic	Cement	Euhedral	5-20	Black	...
Quartz Cement 2	Various	Cement	Various	2-50	Bright Blue	Homogeneous
Dolomite 4	Micritic	Cement	Anhedral	1-3	Light Pink	Mottled

Table 1. Sedimentological description and mineralogical composition of each event comprising the combined paragenetic sequence presented in Figure 13.

Sample #	$D13C_{VPDB}$	D^{18}_{OPDB}	$^{87}Sr/^{86}Sr$	Paragenetic Context D3 %	RD2 %	RD3 %
UPH 493	-5.91	-3.50	0.708997	0	50	50
UPH 521 pebble	-4.79	-4.57	0.709576	0	80	20
UPH 521 laminae	-5.75	-5.24	0.711483	0	68	32
UPH 522 dull	-5.26	-4.63	0.709123	0	80	20
UPH 524	-5.87	-4.85	0.709978	30	70	0
UPH 583	-3.00	-5.55	0.709128	50	50	0
LQ 4D	-4.83	-4.51	0.709153	33	55	
LQ 6J	-4.95	-4.60	0.708957	10	10	80
LQ 9I	-5.69	-4.60	0.710240	?	?	?
LQ 14H	-4.98	-4.34	0.708923	?	?	80
SW 7511	-5.23	-5.28	0.708824	0	65	35
SW 7513	-6.06	-5.54	0.708710	0	40	60
SW 7515	-5.86	-4.87	0.708593	50	50	0
SW 7664	-8.40	-3.51	0.708612	30	30	40
SW 7679	NA	NA	0.709330	10	12	78

Table 2. Isotopic composition of the paragenetic sequence (Fig. 13) comprising the Shakopee, Everton and St. Peter lithologies.

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APPENDIX A: CATHODOLUMINESCENT OPERATION

Operating the Relion Cathodoluminescence Stage (Fig. 24)

Make sure vacuum valve between stage chamber and vacuum hose is turned counter clockwise so the valve is perpendicular with the hose (chamber is closed off to vacuum)

1.Turn on the vacuum pump on the floor.

2. Let the vacuum pump for 20-30 minutes while you;

Set up the computer, turn on the camera switches (2), arrange your notes, get coffee, etc. Once it has pumped for 20-30 mins, turn on the Main Power on the control box.

3. Load the sample(s) in the tray. Make sure rock side is up.

4. Close the vent valve and then the sample drawer. Open vacuum valve (clockwise) so it is parallel with vacuum hose. Make sure you hold the stage with other hand while you turn valve.

5. Let the vacuum pump down until at least 100 mTorr. If the vacuum does not pump down check vent valve on the top, front, left corner of the stage and make sure it is closed very tight. Also, you can vent chamber, and check the O-ring around the drawer to make sure it is clean. You can apply vacuum grease to it but apply very conservatively. If chamber still does not pump down to optimal level, check hoses and seals with acetone on Q-tip. At a leak, acetone will cause a brief, rapid decrease in vacuum mTorr level.

6. Make sure the High Voltage dial is at zero.

7. Turn the top dial to Manual

8. Turn on the High Voltage by depressing the red button to the right of the dial.

9. Slowly increase Kv while watching to make sure the Overload button doesn't start to blink.

10. Once Overload button begins to blink turn back Kv dial until it stops flashing.

11. Wait for the pressure to continue decreasing.

12. You can Increase the high voltage dial until at ~7-8 Kv to increase the cathodoluminescence out put, however, many carbonates will luminesce at optimal levels around 4-5 kV.. Silicicalstics, igneous, and metamorphic rocks generally include minerals that require voltage at 7-8kV.

13. Overall, the best working conditions are around 30 mTorr and 500 mAmp.

14. Use the stage dials to adjust your sample to where it needs to be under the scope.

15. Use the magnetic slider to adjust the location of the beam onto the sample.
16. Check out your samples and locate areas of interest.
17. Turn the microscope eyepiece area clockwise when you'd like the image to be shown on the computer.
18. Refocus the image on the microscope and adjust the timing of the image recording on the secondary keyboard.
19. Use the Grab function to take pictures. (Grab, Capture, Selection, select the area of the image you want, File, Save as)

Switching Samples in the CL Scope

(If working in Regulated, turn dial to Manual and begin with #1)
1. Turn down high voltage to baseline (~1.3 Kv)
2. Turn off high voltage button.
3. Turn dial to Pump.
4. Move vacuum pump hose to perpendicular to flow (i.e. Elimate vacuum pressure from stage box).
5. Release vent valve on front left of stage. (DON'T REMOVE FULLY)
6. Open up the drawer.
7. Switch out your samples.
8. If optical is too close, raise up slides with metal stands found in the extra parts kit on the shelf.
9. Close sample drawer.
10. Close vent valve TIGHTLY.
11. Turn vacuum pump hose regulator knob to parallel to flow. (i.e. Allow vacuum pressure to enter box).
12. Wait until pressure is down to 100 mTorr.
13. Turn dial to Manual.
14. Turn on High Voltage
15. Follow steps from #9 on How to turn on the CL Scope.

To Power Down the CL Scope

(If working in Regulated, turn dial to Manual and begin with #1 or Pump and begin with #3)

1. Turn down high voltage to baseline (~1.3 Kv)
2. Turn off high voltage button.
3. Turn dial to Pump.
4. Move vacuum pump hose to perpendicular to flow (i.e. Elimate vacuum pressure from stage box).
5. Release vent valve on front left of stage. (DON'T REMOVE FULLY)
6. Open up the drawer.
7. Switch out your samples.
8. Turn off Main Power on bottom right of control box.
9. Close valve so it's perpendicular to flow.
10. Turn off the vacuum pump on the floor.
11. Vent the chamber with the sample drawer open. (I.e. open vacuum valve, allow atmospheric pressure to enter, CLOSE vacuum valve)
12. Make sure the vacuum valve is perpendicular to flow... ie CLOSED!
13. Close sample drawer.
14. Double check that the vacuum valve is perpendicular to flow, and very well closed!!

Regulated Setting

If the vacuum pumps down too low there won't be enough pressure to have the beam exist. Usually that will happen lower than ~15-20 mTorr. You can control the pressure issue either with the vacuum pump regulator valve or the regulated setting.

Also, if your sample is very gassy and the pressure keeps spiking, using the regulated setting can be useful.

HOWEVER: Almost all sampling can be done easily without the regulated setting.

Background Baseline Regulated Setting

33.5 mTorr, .069 current, .500 mAmps, 8.0 Kv

To go from Manual to Regulated:

Make sure you are at 30-40 mTorr, that you are .400 mAmps or lower and that your Kv is around 8.0

Turn the dial from Manual to Regulated.

From this setting, allow the pressure and current to adjust. From here on out the pressure will adjust for changes in currents or Kv.

If you need to reset it. (No idea why'd you do that.)

1. Make sure the current is ~.100 - .200
2. Turn dial from Manual to Regulated
3. Manually change current using the Solenoid knob. Move it clockwise until back up to .5 mAmps
4. Use a very light hand, it takes a LONG time and will have a signature jump once the valve opens.
5. Hold window switch. It should be close to zero (-1 to 2)

Trouble Shooting/Side Notes

1. If you see many blue/green pin prick sized dots on the screen in CL but not in PL, it could be the grinding powder that many people use. MAKE SURE YOUR SAMPLE IS CLEAN.
2. If the beam isn't falling on the sample, or you want a thin section sized area to react, or the beam isn't concentrated enough, use the magnet slider and magnets to alter the shape, size and location of the beam.

IMPORTANT NOTE: Use your eyes to LOOK at the physical thin section or sample while you adjust the beam. Otherwise you can burn up the sample or crack the thin section.

3. If the beam is WAY off, use the alan wrench near the stage dials to loosen up the stage and adjust to where it should be.
4. If you just want to look at sand grains, load them into the 6 sample holder metal aparatus in the extra parts box. Load the samples like usual. Use plain light and the sample holder circle with the hole cut out to adjust the focus on the rim of the metal. Then switch over to CL to check out the samples in the other five beds.

5. When loading tiny hand samples, remember the beam is coming from the right hand side, so put the shortest samples closer to the beam and the taller samples toward the back (left of the stage drawer).
6. When replacing the cathode, you'll need to condition it. It will arc and the pressure will continually jump all over the place. If this is the case, turn off the pressure regulator at the top of the control box. Leave the beam on at .5mAmps for about a half hour and then set up the Kv to 8 for another half hour or so. Turn the pressure regulator back on and see if it jumps. If it does, repeat the process until the cathode has been conditioned.
7. For now (this may change SOON), the plug for the microscope is connected to the control box. Turning off the high voltage will allow the PL to turn on. It is sort of useful, but would be better if we moved the plug to back into the wall so we can have both the PL and the CL at the same time for references.

If you don't know exactly what you are looking at "Cathodoluminescence of Geologic Materials" is a most excellent source.